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Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International. Held in Atlanta Georgia on June 19-21, 1989. Technical Papers

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Abstract: As a result of the high level of interest in innovative hazardous waste control technologies, U.S. EPA's Office of Solid Waste and Emergency Response and Risk Reduction Engineering Laboratory jointly conducted this conference. The conference consisted of presentations of technical papers and posters by international and domestic vendors of technologies for the treatment of waste, sludge, and contaminated soils at uncontrolled hazardous waste disposal sites. The purpose of the 2 1/2 day conference was two-fold: to help introduce promising international technologies through technical paper and poster displays; and to showcase results of the U.S. EPA Superfund Innovative Technology Evaluation program technologies in addition to other domestic innovative technologies. Both were aimed at increasing awareness of the user community in technologies ready for application. The compendium does not include all papers that were presented; only those that were made available by authors and their institutions are included.

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Office of Solid Waste and
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September 1989

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Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International

Atlanta, Georgia

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Technical Papers

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FOREWORD

As a result of the high level of interest in innovative hazardous waste control technologies, U.S. EPA's Office of Solid Waste and Emergency Response (OSWER) and Risk Reduction Engineering Laboratory (RREL) jointly conducted this conference. The conference consisted of presentations of technical papers and posters by international and domestic vendors of technologies for the treatment of waste, sludge, and contaminated soils at uncontrolled hazardous waste disposal sites.

The purpose of the 2½-day conference was two-fold: to help introduce promising international technologies through technical paper and poster displays; and to showcase results of the U.S. EPA Superfund Innovative Technology Evaluation (SITE) program technologies in addition to other domestic innovative technologies. Both were aimed at increasing awareness of the user community in technologies ready for application.

This compendium does not include all papers that were presented; only those that were made available by authors and their institutions are included. A publication containing one-page abstracts of each presented paper will be available from EPA's Center for Research Information (CERI) in the Fall of 1989. Subsequent inquiries may be addressed to CERI, P.O. Box 12505, Cincinnati, OH 45212.

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EXPERIENCE WITH THE HARBAUER PB3 SOIL CLEANING SYSTEM

Dr. H.D. Sonnen, W. Gröschel, M. Nels

1. SUMMARY

The system to be described is an extractive soil washing system, the HARBAUER PB3, which since July 1987 has been in operation at the former Pintsch oil refining facility in Berlin.

To date 20,000 tons of soil from the Pintsch site itself and from other selected sites has been cleaned by the unit. Experiences and results from these soil extraction operations will be described as well as future plans for the application and use of the technology.

2. INTRODUCTION

Parts of the Pintsch site are heavily polluted from residues of former used oil refining activities.

The primary pollutant groups which were found in both soil and ground water were: Mineral Oil, Halogenated Hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Aromatic Hydrocarbons and Phenols.

In addition Polychlorinated Dibenzodioxine and Dibenzofuran were found at specific locations.

In order to control the immediate danger and limit the release and spread of contamination through dust and air emissions as well as further contamination of the ground water, the Senate of Berlin initiated a clean-up program in the fall of 1984 under the auspices of the Senator for City Planning and Environment (2).

The firm KEMMER/HARBAUER was responsible for the majority of the clean-up activities on the site. Major activities included (4):

- Demolition of contaminated buildings, stacks, and other equipment using maximum level protective clothing.

- Excavation of soil, removal of existing tanks and equipment, and digging out and removal from overflow trenches and ditches. (work was carried out in maximum as well as in lower levels of protection including the use of special earth moving equipment which was equipped with a pressurized air filtered cabin)

- Providing decontamination stations and protective clothing for all employees and vehicles.

- Design, building and operation of a ground water treatment plant.

- Design, building and operation of a soil cleaning plant.

The soil cleaning facility has been in operation since July 1987 and has, in the framework of a Demonstration project under the auspices of the Berlin Senators for Building Construction, successfully cleaned 20,000 tons of soil.

EXCAVATION OF CONTAMINAITED SOIL

SITE CLEAN-UP IN PROTECTIVE CLOTHING

3.0 THE HARBAUER EXTRACTIVE SOIL CLEANING SYSTEM

The soil washing system developed by HARBAUER is the result of a scientific research program in combination with years of practical experience on-site. The unit is capable of cleaning contaminated soil and rubble so that the cleaned material can be refilled on site and is suitable for further unrestricted/normal use. The contaminant is washed out of the polluted material and carried away in the liquid/extractant phase. The process gases and effluent handling systems of the soil washing facility prevent contaminant from being transferred to water or air media.

Each soil washing technology has its own critical cut-off point in the small particle size range where the process can no longer effectively treat contaminated material. Those particle sizes smaller than the cut-off point cannot be economically cleaned and are found in the residual sludges from the washing process. The advantage of the HARBAUER technology is that the cut-off point is at 15 µm, which means that not only scrap/metals, gravel and sand but also silt can be cleaned.

3.1 DESCRIPTION OF THE PROCESS

The principal process steps of the HARBAUER system can be seen in the flow diagram of the plant (FIG. 1). The facility is divided into four basic operations:

- Soil preparation and extraction or clean-up
- Clean-up of process waters
- Treatment/dewatering of remaining sludges
- Removal and cleaning of exhausted air emissions

In the Soil preparation/extraction step (process unit 1) the contaminated soil and rubble is screened and mixed with extractant then subjected to intense vibrations or oscillations produced by the use of mechanical energy which set the material in motion and free the contaminant from the soil particles. It can then be dissolved in the liquid phase thereby forming an emulsion of contaminant with the extractant. The effect of the energy can be enhanced by the addition of cleaning agents (eg. biologically degradable detergents).

Through multi-step rinsing, separation and dewatering operations the cleaned soil particles are recovered from the extractant medium and removed as clean product. The lower particle size limit for separation is 15 µm and as such REPRESENTS THE STATE OF THE ART FOR SOIL WASHING.

Operational costs and requirements for extraction, separation and dewatering increase disproportionately with decreasing particle size. HARBAUER is now investigating, under a joint research project with the Ministry for Research and Technology and the City State of Berlin whether it is technically and economically feasible to achieve an even lower particle size cutoff.

Following the extraction step the dislodged pollutant is found partly as particles and partly emulsified or dissolved in the water phase. The dissolved/emulsified contaminants are carried to the water treatment plant (FIG. 1, unit 2) where they are concentrated out using the following four step process:

- Oil Separation
- Flotation
- Desorption
- Filtration and adsorption on activated carbon

The contaminants removed during the water treatment process are removed as oily sludges, flotation sludges and loaded activated carbon.
The particulate contaminant is recovered together with the fine particle sludge fraction (under 15 µm) and is dewatered with a filter band press. (FIG 1, unit 3). The amount of residual sludge is dependent upon the particle size distribution of the input material and for the soils processed to date is between 5% and 10% of the input.
The degree of pollution of the residual sludge is ultimately determined by the contaminants in question. Low solubility contaminants such as heavy metals enrich the sludge phase whereas high solubility contaminants (organics eg., benzene) result in moderate levels of sludge contamination.

The remaining sludge is currently landfilled but investigations are underway to other more suitable treatment methods (eg. chemical, thermal, solidification).

Light materials in the soil such as tar, wood, roots and charcoal particles will be separated by upward current classification/fluidized bed sorting and screening using a DSM screen.

Because of environmental and worker safety reasons the first three process steps, units 1-3, have an air removal system which feeds the contaminated exhaust air directly into the air cleaning unit (unit 4). Air emissions are cleaned in a two step process using wet scrubbers followed by activated carbon.
In this step any separated volatile materials are recovered as solvent mixtures with incineration as the indicated method of disposal.

In the event that a planned crushing unit is added it will be necessary to have a dry air cleaning system (dust filter) to collect emissions. These residues could then be treated by solidification.

3.2 PROCESS FLOW CHART

The flow chart for the HARBAUER process is shown in FIGURE 2. The contaminated soil is brought by a front end loader to the receiving area after which it passes through an over-sized particle screen where material larger than 60 mm is removed. This step separates materials such as debris, wood, and other miscellaneous large objects which may, depending upon the type and level of contamination, require special disposal.

The debris free soil is then mixed with water in a blade washer where lumpy material is broken up by the stirring motion. In the same step light material (wood particles, charcoal and tree roots) are separated out. This light particle fraction is temporarily stored in containers.

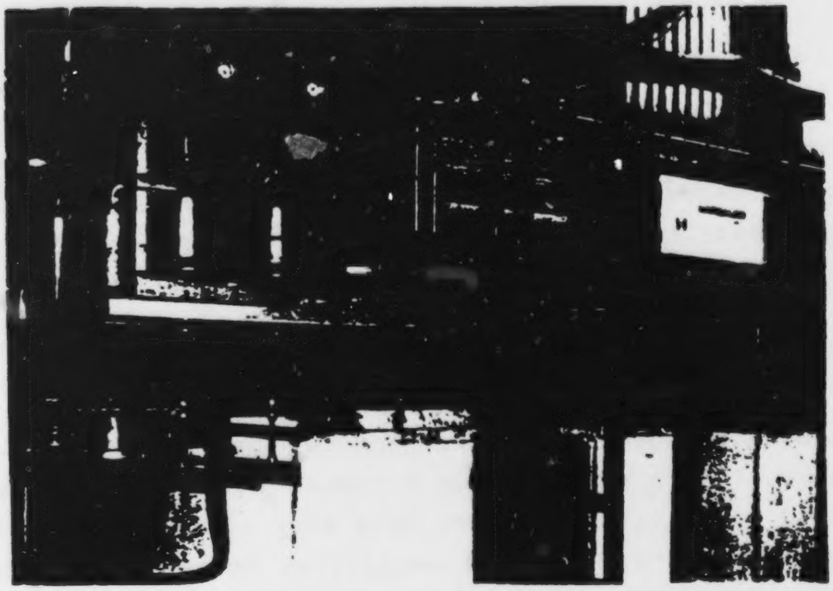
The majority of the material from the blade washer goes into a two step screening process. Material from the first screen (greater than 5 mm) is rinsed, dewatered and removed as clean material. The overflow from the second screen goes into the extraction unit for further treatment. The washed-out fine material greater than 15 µm is concentrated in hydroclyclone I and is ultimately brought to the extraction unit.

The actual extraction of the soil occurs in a specially developed extraction unit. Here a forward screw is subjected to axial vibration, created by an electronically steered mechanical energy component. In this extraction unit the particles between 15µm and 5mm are cleaned using mechanical energy. The soil particles are subjected to an energy density sufficient to break the bonds between the contaminant and soil particle so that the contaminant is freed and dissolved in the extractant (water) phase. The frequency, and amplitude of the energy can be varied to optimize conditions for the individual types of pollutant and soil being treated. The extractant, which is generally water (sometimes with small amounts of biologically degradable detergent), is added in a 1:1 ratio to the soil (1,3).

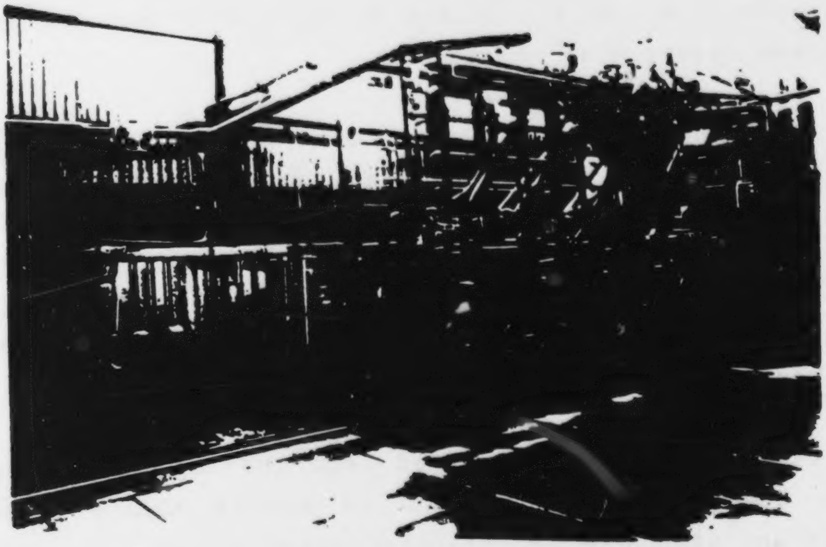
In the next step the material is washed in a countercurrent sandtrap. Here the fine fraction < 130 µm and its extractant is freed of any light material like wood, charcoal, or tar using a sieve and is carried to the fine particle wash.

The larger material (sand/fine gravel fraction) is dewatered in sieve III and sent to the fluidized bed sorter. Here the contaminated "light" materials are floated out and removed from the washing process by a screen.

The clean-up of the fine particle fraction occurs in a five step countercurrent hydrocyclone. Following the hydrocyclones the dewatering of this material stream together with the sand/fine gravel fraction which was the throughput of the fluidized bed sorter occurs in sieve IV. Cleaned material is carried out by a conveyor belt.



EXTRACTION UNIT AND HYDRAULICS



MULTI-STEP HYDROCYCLONE UNIT

The over flow of hydrocyclone unit I contains the fine particle fraction under 15µm, in which the contaminant may in some cases be concentrated. The separation of these solids from the process water stream is accomplished by thickening. The sedimented sludge is then dewatered using a filter band press.

The solid free process water is then cleaned together with the contaminated ground water. The ground water/process water treatment plant is a 4 step process. First any oil layers are removed by an oil separator. This step is followed by flotation where heavy metals and and emulsified hydrocarbons are separated by addition of the appropriate chemical agents.

The primary pollutant group in ground water at the Pintsch site is volatile chlorinated hydrocarbons. To achieve recovery of volatiles an air stripping step was added which has a recovery efficienly of approxmately 99 %. The stripped volatiles are recovered from the air stream by activated carbon. The carbon is steam regenerated on-site.

The last step of the water treatment process consists of a series of filters including three sand filters followed by six activated carbon filters. Input to the filters can be individually controlled for selective loading depending upon the contaminant stream in question. Here the remaining trace amounts of contaminant are removed. The cleaned process water is then recirculated through the soil cleaning process.

The cleaned groundwater is fed into the adjacent waterway, and must therefore be monitored to ensure that it meets the stringent standards for drinking water purity.

4.0 CLEAN-UP RESULTS

To date the unit has treated soils from the following sites:

Site of former chemical production/refining companies,

- Waste oil refining facility
- Tar chemistry facility
- Paint fabrication facility

The primary pollutants found in these facilities were:

Hydrocarbons
Chlorinated Hydrocarbons
Aromatic and Polyaromatic Hydrocarbons
PCBs
Phenols

Sites of former gas works,

- HKW Moabit, Berlin
- Eisstadion Wilmersdorf, Berlin

Primary Pollutants for these sites were:

Hydrocarbons
Polyaromatic hydrocarbons
Phenol
Cyanides

Sites contaminated by Mercury

- Soil from the former chemical plant at Marktredwitz

The clean-up results for these various sites can be seen in figures 3,4,5.

5.0. FURTHER DEVELOPMENT

Using the outlined systematic solution it is possible to clean soil with complex pollutants and problematic particulate composition in such a way that the cleaned soil may be refilled and reused.

We now have experience and results from a relatively broad range of sites (former chemical/physical facilities, gasworks, and heavy metal contaminated soil). Nevertheless there is still a need for further research and development to evaluate the total picture for abandoned site clean-up; in light of the non-homogeneous nature of these sites and the unique character of each clean-up problem.

The actual potential for development lies in the treatment of the fine and medium clay fraction (material with particle sizes under 15µm) and in improving the separation, clarification, dewatering and transport aspects.

Based on the positive results of the PB1, PB2 and PB3 one should be able to assume that at the end of the current development phase (the final development of the PB4) one should have a system capable of handling the majority of abandoned sites in a systematic way using an environmentally safe and economically feasible technology.

6.0 LITERATURE

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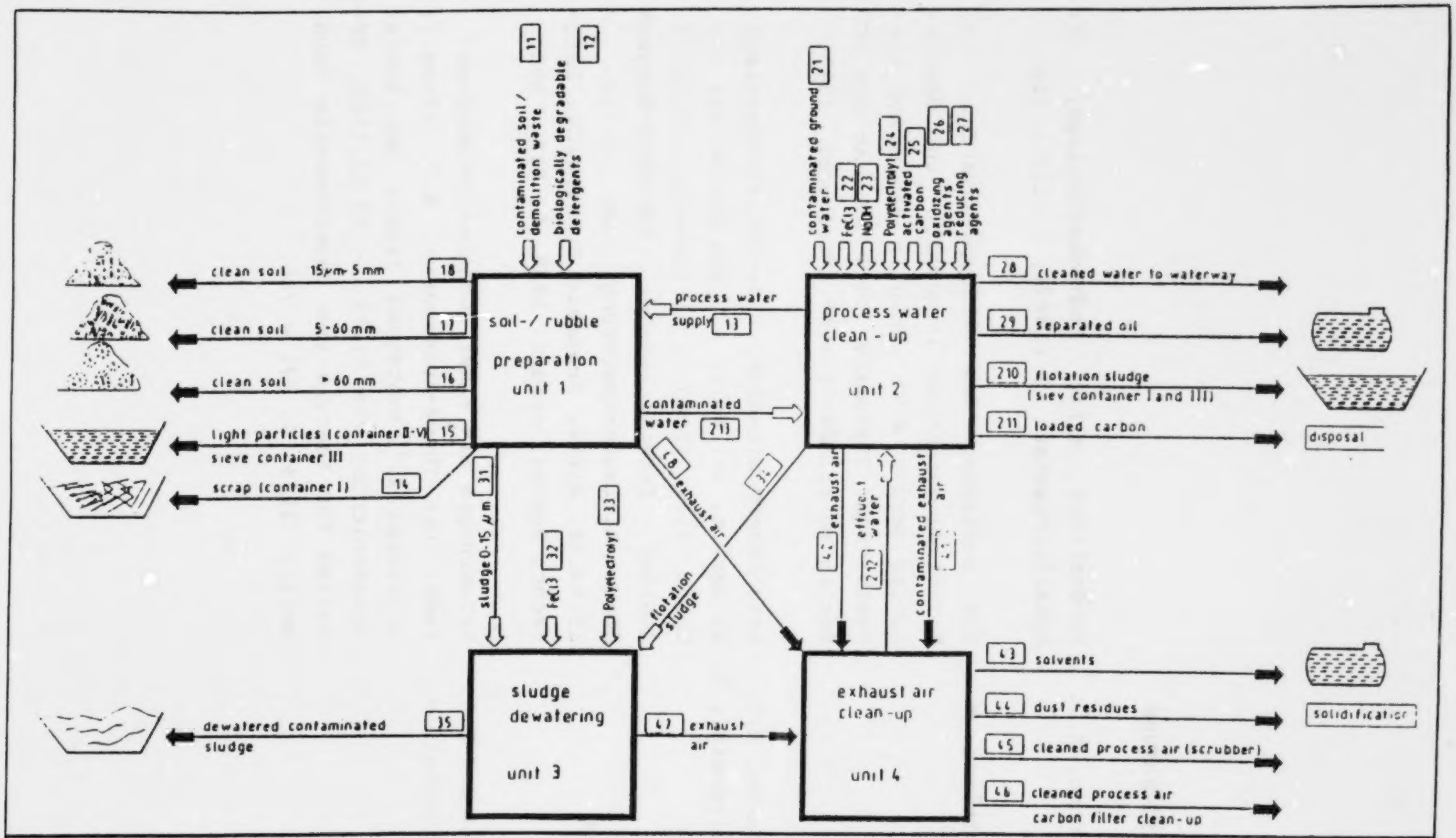
contaminated soil / demolition waste
11
biologically degradable detergents
12
contaminated ground water
21
FeCl3
22
NaOH
23
Polyelectrolyt
24
activated carbon
25
oxidizing agents
26
reducing agents
27
clean soil 15µm-5mm
18
clean soil 5-60mm
17
clean soil >60mm
16
light particles (container II-V)
15
sieve container III
scrap (container I)
14
soil-/rubble preparation
unit 1
process water supply
13
contaminated water
211
process water clean - up
unit 2
28
cleaned water to waterway
29
separated oil
210
flotation sludge (siev container I and III)
211
loaded carbon
disposal
31
sludge 0-15 µm
FeCl3
32
Polyelectrolyt
33
48
exhaust air
34
flotation sludge
42
exhaust air
effluent water
212
contaminated exhaust air
41
sludge dewatering
unit 3
35
dewatered contaminated sludge
47
exhaust air
exhaust air clean-up
unit 4
43
solvents
44
dust residues
45
cleaned process air (scrubber)
46
cleaned process air carbon filter clean-up
solidification

Figure 1: Material Flow Diagram Soil-/Rubble Preparation Plant

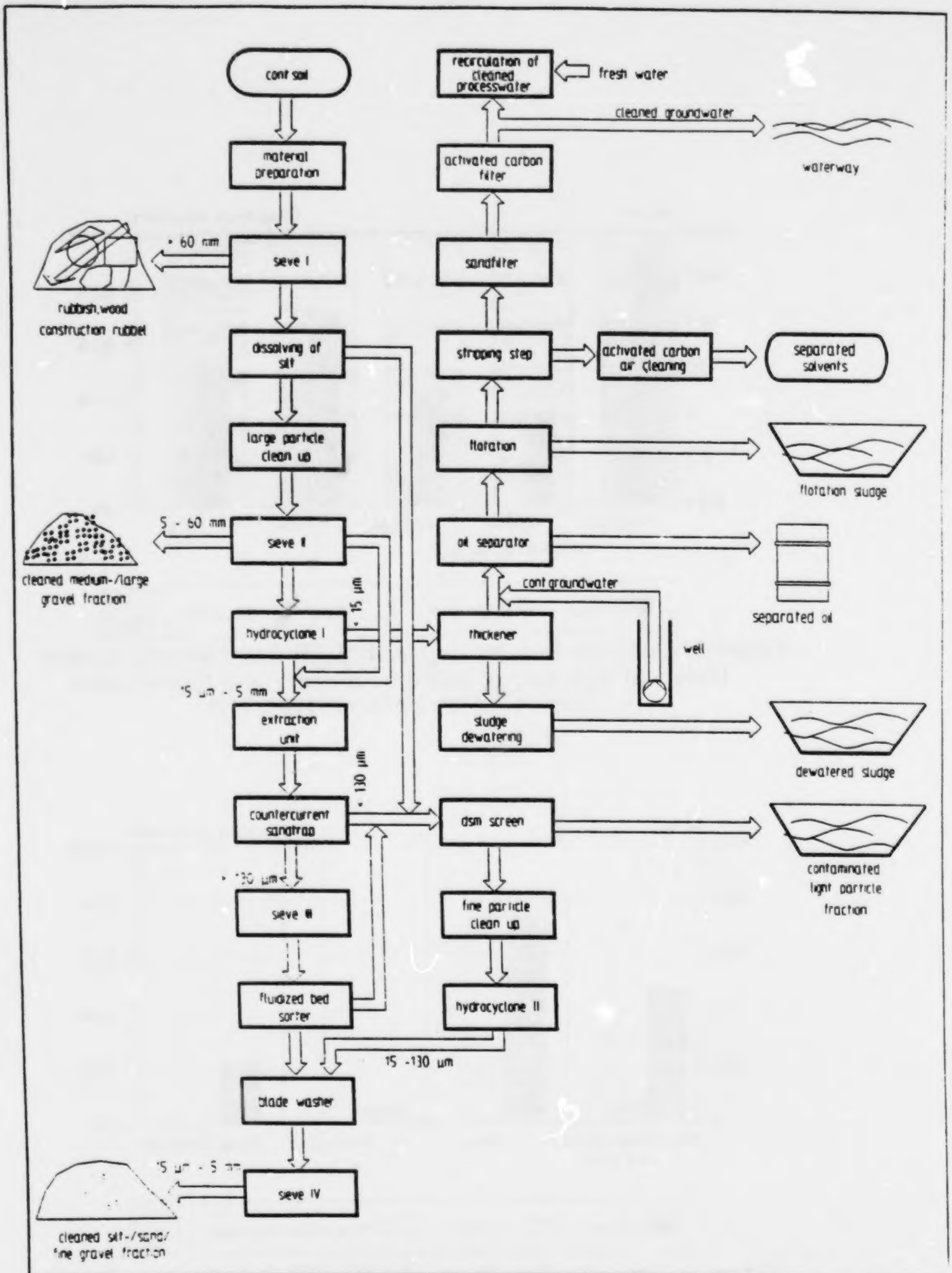
cont soil
material preparation
> 60 mm
sieve I
rubbish, wood construction rubbel
dissolving of silt
large particle clean up
5 - 60 mm
sieve II
cleaned medium-/large gravel fraction
< 15 µm
hydrocyclone I
15 µm - 5 mm
extraction unit
< 130 µm
countercurrent sandtrap
> 130 µm
sieve III
fluidized bed sorter
15 -130 µm
blade washer
15 µm - 5 mm
sieve IV
cleaned silt-/sand/ fine gravel fraction
recirculation of cleaned processwater
fresh water
cleaned groundwater
waterway
activated carbon filter
sandfilter
stripping step
activated carbon air cleaning
separated solvents
flotation
flotation sludge
oil separator
separated oil
cont groundwater
well
thickener
sludge dewatering
dewatered sludge
dsm screen
contaminated light particle fraction
fine particle clean up
hydrocyclone II

Figure 2: Block Diagram System HARBAUER Groundwater- and Extraktive Soil Claening on the former Pintsch Site, Berlin

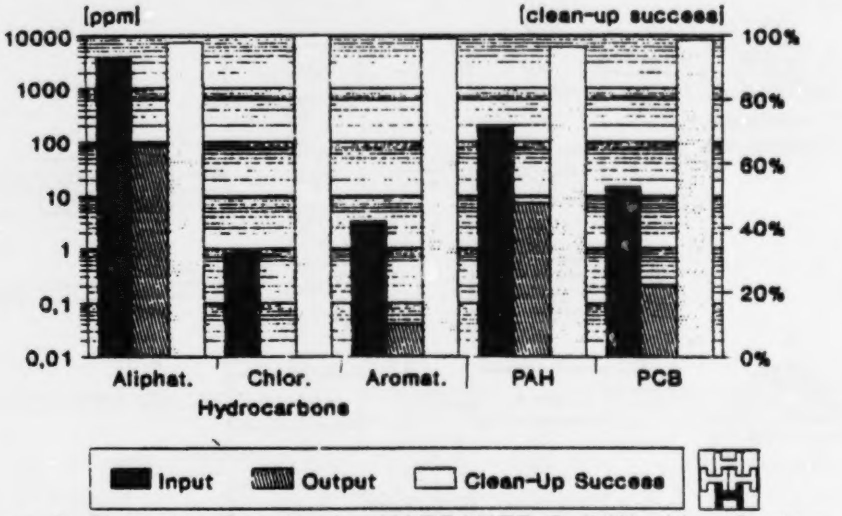

Figure 3: Clean-Up Results for HARBAUER Soil Washing System (Origin of soil: former waste oil refinery and former paint manufacturing plant, respectively)

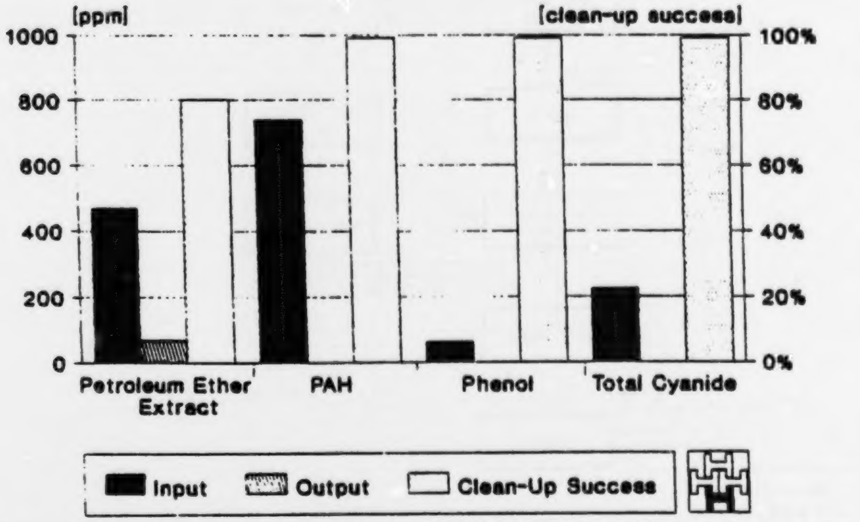

Figure 4: Clean-Up Results for HARBAUER Soil Washing System (Origin of soil: former gasworks site)

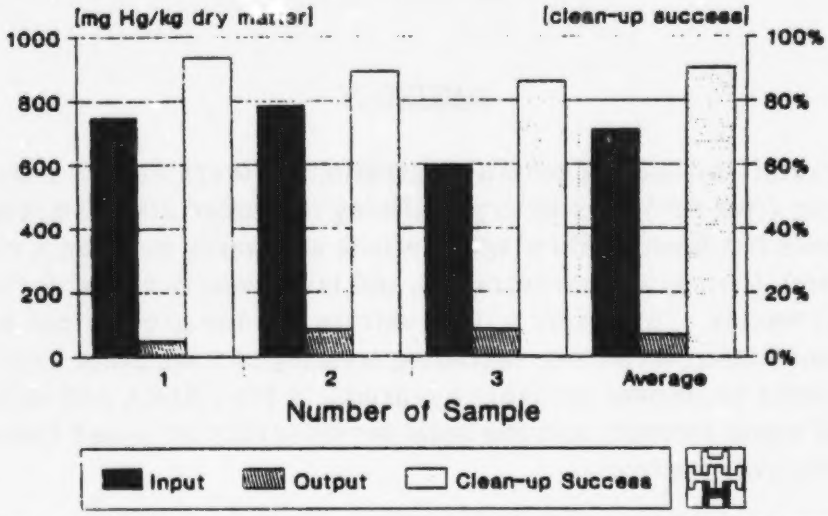

Figure 5: Clean-Up Results for HARBAUER Soil Washing System
(Origin of soil: former chemical plant site A)

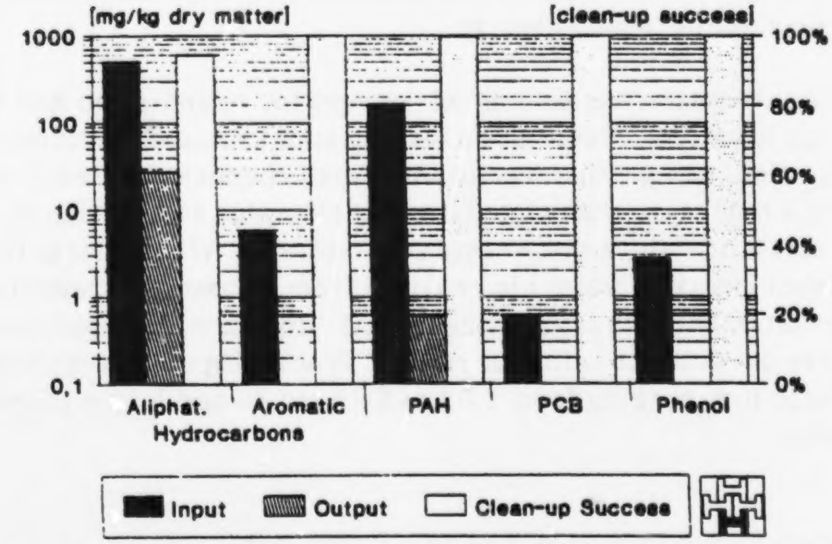

Figure 6: Clean-Up Results for HARBAUER Soil Washing System
(Origin of soil: former chemical plant site B)

FREEZE TECHNOLOGIES CORPORATION

REMEDIATION AND TREATMENT OF RCRA HAZARDOUS WASTES BY FREEZE CRYSTALLIZATION

ABSTRACT

Freeze crystallization is a general separations process used to remove pure components from solutions by crystallizing the materials to be removed. This process has been used for applications as diverse as organic chemical refining and fruit juice concentration, and is especially suited for treating hazardous wastes. This paper will illustrate how the process can be used in site remediation activities, including treating contaminated soils, where it can be used to recover valuable by-products from RCRA and other industrial waste streams, and the basis for its utility in mixed (hazardous and radioactive) wastes.

Freeze Technologies Corp. has built a mobile site remediation prototype commercial plant to demonstrate the field remediation aspects of this technology. The capacity of the unit is nominally 10 gpm of ice production from a leachate or groundwater, at 90% water recovery. It is contained in two modules that are transported on standard low-boy trailers, and requires less than 1 week to set up.

Freeze crystallization has several advantages for remediation and waste recovery applications. First, it is a very efficient volume reduction process, producing a concentrate that has no additional chemicals added to it - if disposal in a hazardous waste landfill, or incinerator destruction is required this will reduce these costs substantially. When a large fraction of the solvent (usually water) is removed from a waste, the remaining impurities often begin to crystallize as well - they are often sufficiently pure to have by-product value for resale. Processing costs with freezing are generally low, ranging from $.03 to $.15 for 40 and 5 gpm plants, respectively.

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FREEZE PROCESS DESCRIPTION

The basic operation involved in freeze crystallization is the production of crystals by removing heat from a solution. Crystals produced in this manner invariably have very high purities. Once small, uniform crystals have been produced, they must be washed to remove adhering brine. The brine is recycled to the crystallizer, so that as much solvent as desired can be recovered. The pure crystals are usually melted in a heat-pump cycle, which further improves the energy efficiency of the process.

When one or more of the solutes exceeds its solubility additional crystal forms are produced, but they are formed separately from each other and from the solvent crystals. Since in most waste applications the solvent is water, and ice is always less dense than the solution and the solutes usually more dense, it is easy to separate these crystals by gravity.

A freeze crystallization process is then composed of the following components, as illustrated in the process flow diagram of Figure 1:

- a CRYSTALLIZER, where heat is removed to lower the temperature of the material to the freezing temperature of the solution (usually crystallizing the solvent first);
- a EUTECTIC SEPARATOR to segregate the crystals of solvent and solute into different streams, so that each can be recoverd in pure forms;
- CRYSTAL SEPARATOR/WASHERS that function to remove the crystals from the mother liquor in which they are slurried, and to wash adhering brine to very low levels so that the recovered crystals have high purity;
- a HEAT-PUMP REFRIGERATION CYCLE to remove refrigerant vapor from the crystallizer, and compress it so that it will condense and give up its heat to melt the purified crystals;
- HEAT EXCHANGERS are used to recover heat from the cold effluent streams, improving the heat efficiency of the process.
- DECANTERS and STRIPPERS are required in some processes to remove volatile materials and/or refrigerant from the effluent streams before discharge;
- appurtenant UTILITIES, CONTROLS, ELECTRICAL SWITCH GEAR, PUMPS AND PIPING are required to implement the freeze process in a continuous, closed system.

FREEZE TECHNOLOGIES CORPORATION

The design, operating characteristics, capabilities and limitations are determined largely by the type of crystallizer that is used, of which there are three basic choices:

1) INDIRECT CONTACT, using a scraped surface or similar heat exchanger that will crystallize by removing heat through the heat transfer surface.
2) TRIPLE POINT crystallizers use the solvent as the refrigerant at its triple point (where solid, liquid, and vapor phases are all in equilibrium). For instance, with aqueous systems, the triple point occurs at less than 3 mm Hg. absolute pressure at 30 degrees F, or below.
3) SECONDARY REFRIGERANT freezing uses an immiscible refrigerant that is injected directly into the process fluid, and evaporates at several hundred to several thousand times the vapor pressure of the solvent.

The third option offers a number of advantages in treating hazardous wastes, resulting in a less expensive process that is inherently capable of producing higher quality effluents and effecting a greater reduction of the final volume.

10 GPM REMEDIATION PROTOTYPE

The freeze crystallization process that has been accepted into the EPA's Superfund Innovative Technologies Evaluation (SITE) Program is a secondary refrigerant process. A prototype commercial remediation plant has been designed and built for this program, and is illustrated in the photo of Figure 2. The capacity of the plant is a nominal 10 gpm of ice produced from an aqueous waste stream with a freezing point of 20° F.

The plant contains all of the components described in a typical freeze crystallization process above, including the crystallizer, eutectic separator, crystal separator/washer, heat exchangers, heat pump (open cycle screw compressor), decanters and strippers, and ancilliary utility related systems.

The plant is designed for ultimate transportability, using modular design concepts developed by Applied Engineering Co., Orangeburg, SC, the acknowledged leader in this field. The plant is contained in two modules designed for transport on the back of low-boy trailers. Each measures approximately 50' l x 13' w x 11.5' h. They are picked off upon arrival at the site by a standard road crane, and one placed on top of the other. The three electrical and thirty flanged-piping interconnections take about a day to complete.

The plant is totally self-contained except for electrical supply, containing instrument air, cooling water, electrical distribution, and electrical heating components. It has a distributed digital processor that is programmed to operate without attendance, using on-line quality sensors to evaluate process efficiencies and discern any operating problems, recycling effluent for re-processing if warranted.

S.I.T.E. DEMONSTRATION PROGRAM - STRINGFELLOW NPL

The FTC Direct Contact Secondary Refrigerant Freeze Crystallization Process was accepted by EPA's Office of Research & Development, SITE Program, into the third phase of their program, when first proposed by Freeze Technologies. A program with the State of California, Department of Health Services, Alternative Technologies Office, was already in place, and the selection of the Stringfellow NPL site had been agreed to with the state.

The goals of the SITE program are, among other things, to demonstrate applicability of a technology on as general a waste stream as can be found, and to develop the best economic and performance criteria that can be projected from test results. Freeze Technologies proposed that testing could be performed with either a .5 gpm portable pilot plant or with a 10 gpm prototype remediation plant, designed specifically for Superfund-type work. The groups involved in the demonstration of this technology concurred unanimously that the larger plant is a better vehicle for accomplishing the goals of the program.

The current schedule will have the equipment at the Stringfellow NPL site in late July and installed and ready to operate in early August. The SITE tests and sampling program will occur over a two to three week schedule in August, with a public visitors day on Sunday, August 16, 1989. Further testing for reliability and longer-term performance confirmation will continue into September, and the plant will be removed from the site by the end of September, after appropriate decontamination.

This demonstration program is designed to have minimal impact on the host site, a condition that is paramount in the planning at the EPA Regional level and with local communities. In our case, we will fit the freeze equipment in as a 'black box' in the pipeline that carries wastes from the NPL site to the on-site pretreatment plant. We will intercept the wastes between the collection wells and the pretreatment plant, process the wastes, then recombine them for transfer to the pretreatment plant. The residence time in the freeze crystallization plant, including storage before and after the actual freeze processing equipment, will be 72 hours.

Since the freeze process operates in closed vessels, with recycle of refrigerants and wastes at temperatures well below ambient, there are no emissions from the process. An option exists at Stringfellow for treating the concentrated effluent for metals recovery, for organic by-product extraction, or by solidifying the concentrate for subsequent landfilling. The by-product recovery is an attractive option as it eliminates a large volume that is now landfilled.

WASTE TREATMENT WITH BY-PRODUCT RECLAMATION

Remediation offers some opportunities for by-product recovery, but more frequently these applications occur in on-going RCRA generation facilities. Here we'll discuss, first, the generic conditions that favor freeze crystallization treatment, and how other unit processes can be used with freezing to offer a complete remediation or by-product recovery process train. Then we'll cover a few recent applications we've reviewed and tested using freeze crystallization.

GENERIC APPLICATION CONSIDERATIONS -

Freeze crystallization works by making pure crystals from water, or other components, in a waste solution. The waste must be in liquid form, so contaminated soils are treated by first washing the impurity out of the soil into a wash solvent, usually water. In the case of aqueous based wastes the crystal that is produced is ice, and all impurities are excluded and remain in the concentrated liquid portion. The process is effective in removing water from these wastes, reducing the volume that must be dealt with.

Since crystallization excludes all impurities from the ice, all impurites are equally removed - the freeze process is capable of treating wastes with heavy metals, all types of dissolved organics, and radioactive materials. And **all of the impurities are reduced in concentration in the effluent by a factor of about 10,000.**

Freeze crystallization is not the answer for all applications, and the chart in Figure 3 gives an indication of the conditions that favor it's use over alternative treatment technologies. The chart demonstrates that freezing becomes more economically and technically competitive as the waste becomes more concentrated and more complex. For instance, wastes with heavy metals require concentrations of 1,000 to 10,0000 mg/l to be economically recoverable with freezing. Aqueous streams require organic concentrations of 3 to 7 wt-% before it is more economical to treat with freeze crystallization than by conventional means. Yet, when the waste contains both organics and heavy metals freeze becomes more economical than multi-process treatment trains using conventional technologies at between .5 and 1.5 wt-% total contaminants.

CASE STUDY 1 - Stringfellow Leachates

Treatability studies were performed on Stringfellow leachates with the approximate composition shown in Table 1. These tests confirm that freezing will recover over 90% of the water, concentrating the impurities into a minimal volume for disposal and/or recovery operations. In the treatability tests (methods and equipment described below), crystal clear melt was produced with a reduction in conductivity from 39 mS/cm to less than .02, approaching a ratio of 1000:1. Table 1 also shows anticipated effluent qualities at 90% recovery of water from the leachate.

Currently the leachate from Stringfellow is treated in a conventional system consisting of hydroxide precipitation of heavy metals and activated carbon adsorption of the organics. The sludge is disposed of in a hazardous waste landfill, and the carbon is returned for regeneration. Treatment costs with this scheme are outlined in Table 2. Throughput at Stringfellow has been slowly declining, with current production from the interception wells at about 225,000 gallons per month. The annual cost for only the variable items that can be displaced by treatment with an alternative technology is about $1.2 million.

With freeze crystallization, the operating costs in this size plant are about $.09 per gallon. Costs as a function of treatment plant size are summarized in Table 4. The variable costs using freeze crystallization for treating the Stringfellow strong leachate would total less than $.25 million per year. Depending on amortization rates for the equipment, the annual charge would range from $.2 to $.5 million. Freeze crystallization will also leave a concentrated waste stream of about 1300 cubic yards. Incineration of this might cost as much as $300,000 per year.

CASE STUDY 2 - Mixed Industrial Wastes

Industrial facilities often have wastes that are collected from a variety of places and treated at the end of the pipe. In metal fabrication shops with electroplating, metal cleaning, pickling, stamping, machining, and other operations, the waste coming out the end of the pipe might resemble the analysis shown in Table 3. A typical treatment train might include an oil-water separator, neutralization, hydroxide precipitation, and discharge to a POTW for organics removal. However, municipalities are looking much harder at toxic organic discharges, and often some of the cleaners used in the plant are methylene chloride or other toxic chlorosolvents.

Freeze Technologies has performed laboratory testing on a waste such as this, collected after an API separator. Over 90% of the water was converted to ice. Alkalinity and sulfate salts were precipitated with heavy metals, hardness cations, and probably to some degree with sodium ions. After about 75% water removal a second organic phase began to form, and a significant portion of the influent organics partitioned into this phase that was composed of about 75% organics and 25% water. The water phase contained less than 10% organics, but had most of the dissolved salts.

The organic phase that forms this way will have a high heating value so it can be incinerated directly, or perhaps recovered for its fuel value. The tests in the batch treatability lab showed that this organic layer had a specific gravity much less than ice, and it collected in the top of the ice drain column. This will allow its recovery from a freeze crystallization process by making minor changes in the wash column design.

TREATABILITY TESTING

Within the context of the CERCLA/SARA legislation, and the programs and regulations that the Agency has adopted to implement it's provisions, it seems appropriate to address treatability testing and the impact on new technology utilization in Superfund and other remedial actions. First, given the complex waste matrices normally encountered in the vast majority of remediation sites, Superfund or RCRA remedial actions, treatability studies should always be conducted.

Most Remediation Project Managers realize that soil treatment technologies are sufficiently new, and the wastes so diverse, that treatment feasibility testing is needed, especially with new technologies. But it is amazing how many of these managers labor under the misconception that a wastewater analysis is sufficient to define the optimal treatment train for cleaning up liquid waste streams. At a major tertiary treatment sewage reuse application in the early 1970's, where the effluent was thoroughly characterized, the reuse client wanted to demonstrate the treatment train and reuse application. A 2 month, $150,000 demonstration program turned into a year effort and $1 million expenditure, and resulted in several major equipment innovations and rather drastic modifications to the conventional treatment design criteria.

From our experience with 8 years of development of the freeze crystallization process, and another 10 years of development of environmental process technology, there are a number of guidelines we would propose for treatability testing in EPA Superfund and other industrial waste programs:

1) Treatability studies should always be done by the technology developer, for several reasons. First, the developer is the one who will give process guarantees, and this is one of the necessary steps in giving warranties. Second, the best knowledge of how actual waste characteristics impact process performance is resident in the developers' staff, and expansion of this database is a needed and beneficial part of the Agency's function in the Cleanup of America. And third, the expenditure for treatability studies means nothing if they don't result in better, more efficient, more economical treatment at contaminated sites, and this won't be done without the involvement of the developers.
2) Treatability studies should be incorporated into the RI/FS activities, and replace the paper studies that are currently the basis for selecting between alternative treatment technologies. There are two reasons for getting the developers involved at this stage: their input into technical solutions, and more accurate cost information for the Agency to select between alternative treatment options at a given site. The REMS and ARCS contractors are at best 6 months behind on individual technology development programs, and more frequently 18 to 30 months. The RI/FS process is a way for EPA to effectively help the technology transfer from the developers to their contractors.
3) The EPA and its contractors should not attempt to define the treatment technologies at such sites, but rather should conduct the procurement activities in such a way as to elicit complete strategies from technology developers. Most remediation sites have the need for a variety of treatment technologies. The wastes occur in several media, and the compositon at most sites varies significantly with the location and goegraphy. There is a great deal of networking going on between technology developers, and

the most efficient method for defining treatment trains is to define a clean-up standard and let the individual developers provide the train of technologies for providing that.

The technology developer should have an institutionalized place in the remediation activities of Superfund and private clean-ups. The best process technology is resident in this community, and this resource should be used for its expertise in a way that ensures competition in procurement and full assessment of alternatives. One clear way to provide this, if not the only way, is to procure clean-up strategies on a competitive basis, by writing performance specifications based on ARAR's. Very many ROD's are issued with exceptions to ARAR's without a solid technical basis, which is the only basis allowed by statute. If all bidders of new technologies take exceptions to the ARAR's, then there is a technical basis which is defensible.

Freeze Technologies performs treatability studies in the apparatus shown in the photo of Figure 4. A simplified flow diagram for the unit is shown in Figure 5. The unit operates in a batch mode. Feed is drawn under vacuum into the crystallizer, and recirculation between there and the drain column is started with the slurry pump. Refrigerant is pumped into the crystallizer, where it bois as it is heated by contact with the waste. The refrigerant vapor passes into a refrigerated condenser, condenses, and is pumped back to the freezer. When the drain column is packed full of ice the process is stopped and the ice is washed and melted. The concentrate drains out of the ice back to the crystallizer, and is saved for additional testing. Since only about 50% of the water in any batch can be converted to ice, simulation of 90% recovery requires 4 stages of concentration. Twenty gallons of sample is required to allow 12 of these staged tests.

These tests accomplish the following:

- interactions between refrigerant and waste are observed, such as foaming or emulsification, that must be chemically stopped.
- phase equilibria are confirmed, showing the operating temperatures that will be required.
- the occurance of eutectic crystallization are observed.
- physical properties of the waste at the crystallizing conditions are determined.

The impact of this information is that more detailed preliminary process designs are possible, which in turn allows more accurate cost projections. Problems that would be seen in the field often show up at this stage of testing, and design adaptations made in the batch lab are the first stage in modifying the full scale equipment for use with new applications.

TABLE 1
STRINGFELLOW LEACHATE ANALYSES

Component	Concentration, mg/l Feed	Concentration, mg/l Melt
pH	3.5	6.5
Conductivity, mS/cm	39	.02
Dissolved Organic Carbon	1125	<1.
p-CBSA	1670	<1.
Volatile halocarbons	9.7	< .010
Volatile ketones	14.	< .010
Na	820	<1.
Total heavy metals	3385	<5.
Al	1650	<1.
Cd	2.5	< .010
Cr (+6)	85	< .010
Cu	9	< .010
Fe	335	<1.
Mg	1160	<1.
SO_4	16,200	<5.
Cl	335	<1.
NO_3	320	<1.

TABLE 2
STRINGFELLOW CONVENTIONAL TREATMENT COSTS

Chemicals	$ .015	per gallon
Activated Carbon	$ .027	" "
Supplies	$ .006	" "
Electricity	$ .005	" "
Labor	$ .065	" "
Effluent Post-treatment	$ .098	" "
Sludge Disposal	$ .147	" "
TOTAL - Variable Cost	$ .363	" "

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TABLE 3
INTEGRATED MANUFACTURING END-OF-PIPE EFFLUENT

Waste Component	mg/l Concentration
Total Dissolved Solids	12,500
Dissolved Organics	8,000
pH	10.
Alkalinity	5,000
Sulfates	4,700
Chlorides	1,500
Heavy Metals	3,000

TABLE 4
FREEZE CRYSTALLIZATION COST SUMMARY

COST COMPONENT	COST AT PLANT SIZE, $/GAL		
	5 GPM	10 GPM	40 GPM
Amortization, 5 year SLD	$ .08	$ .05	$ .015
Labor	.04	.02	.005
Electricity	.008	.0075	.006
Supplies, Chem, Etc	.010	.0075	.005
Maintenance	.007	.005	.004
TOTALS	.145	.09	.035

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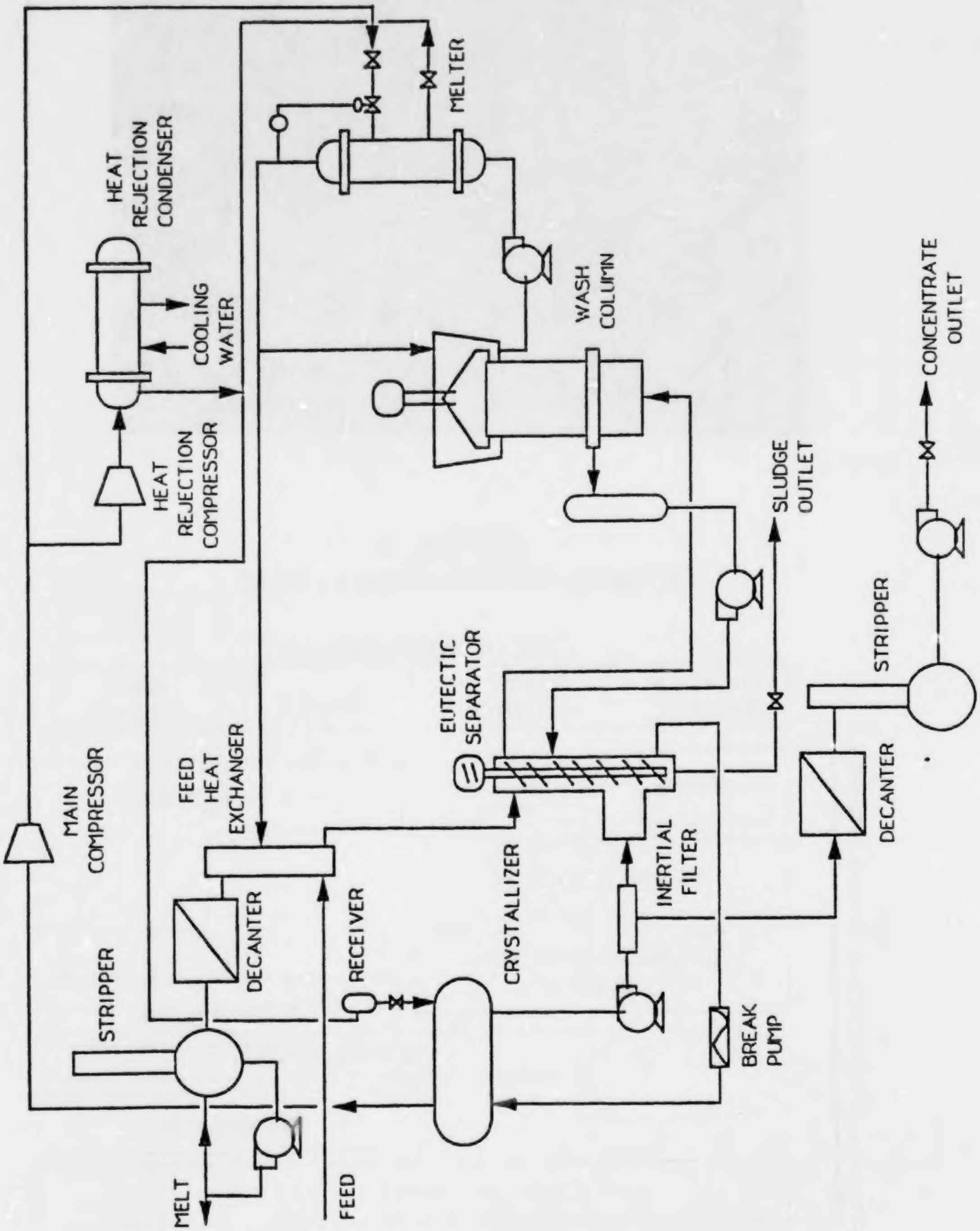
FIGURE 1

FREEZE PROCESS PROCESS FLOW SCHEMATIC


HEAT
REJECTION
CONDENSER
MELTER
COOLING
WATER
WASH
COLUMN
HEAT
REJECTION
COMPRESSOR
SLUDGE
OUTLET
CONCENTRATE
OUTLET
EUTECTIC
SEPARATOR
STRIPPER
MAIN
COMPRESSOR
FEED
HEAT
EXCHANGER
INERTIAL
FILTER
DECANTER
CRYSTALLIZER
RECEIVER
DECANTER
STRIPPER
BREAK
PUMP
MELT
FEED

FREEZE TECHNOLOGIES CORPORATION

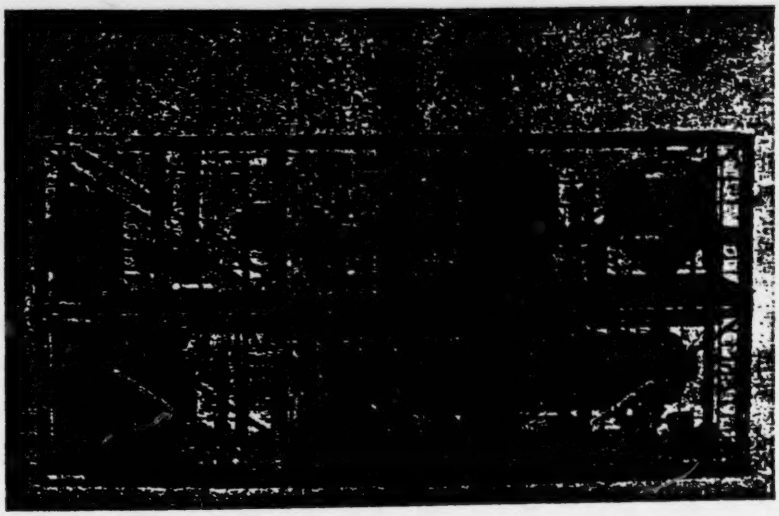


FIGURE 2
10 GPM REMEDIATION PROTOTYPE PLANT

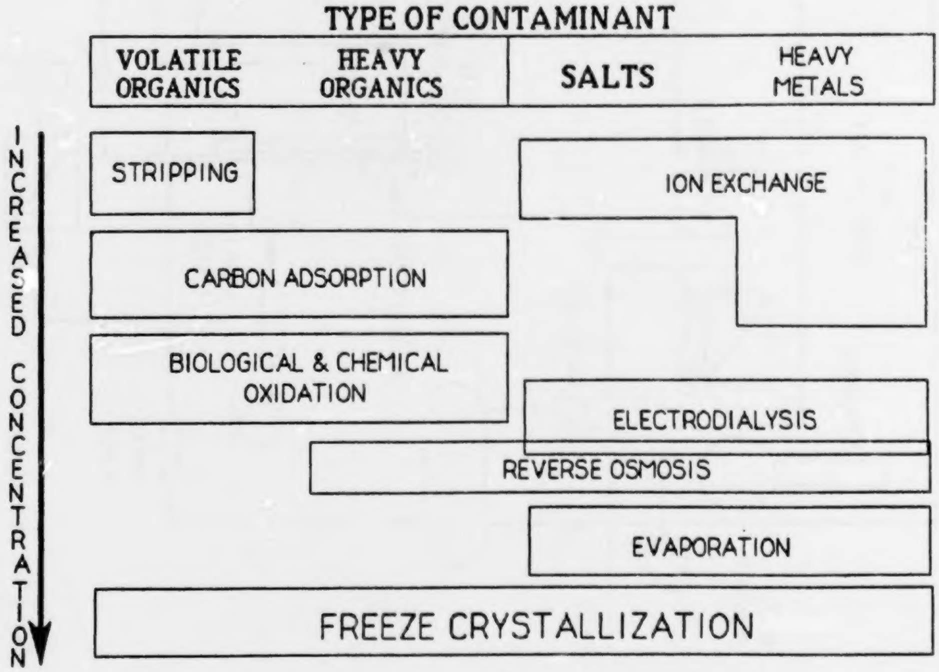
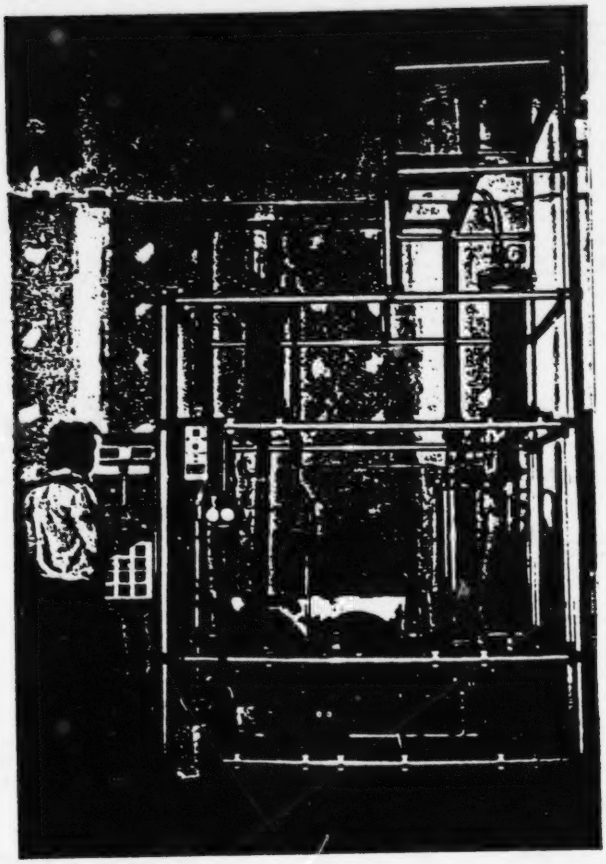

TYPE OF CONTAMINANT
VOLATILE ORGANICS
HEAVY ORGANICS
SALTS
HEAVY METALS
INCREASED CONCENTRATION
STRIPPING
ION EXCHANGE
CARBON ADSORPTION
BIOLOGICAL & CHEMICAL OXIDATION
ELECTRODIALYSIS
REVERSE OSMOSIS
EVAPORATION
FREEZE CRYSTALLIZATION

FIGURE 3
TECHNOLOGY COMPARISON CHART

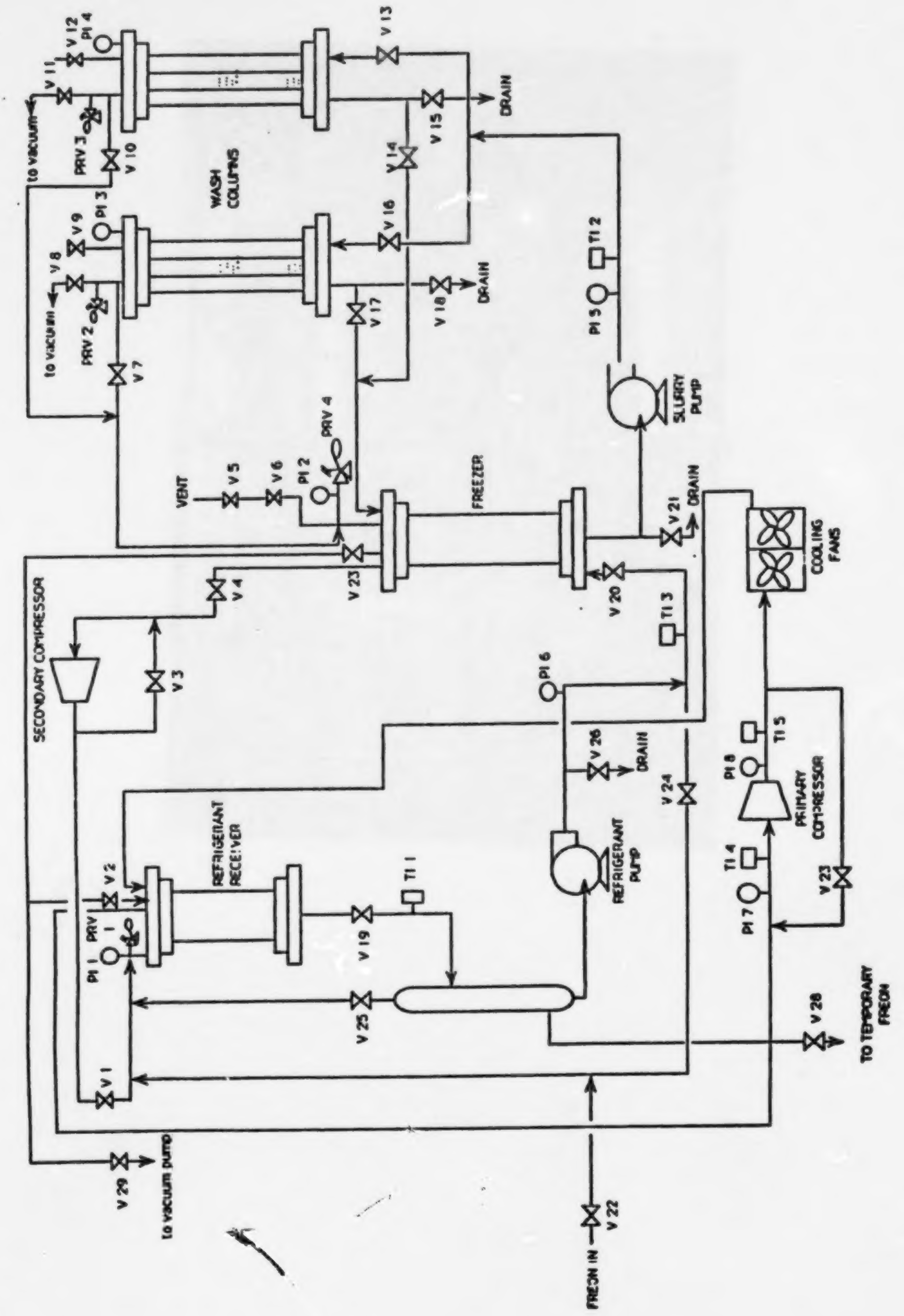
FIGURE 4

BATCH TREATABILITY TEST LABORATORY



FREEZE TECHNOLOGIES CORPORATION

FIGURE 5
BATCH TREATABILITY STAND PROCESS SCHEMATIC


V 13
V 12
PI 4
V 11
to vacuum
PRV 3
V 10
V 15
DRAIN
V 14
WASH COLUMNS
PI 3
V 9
V 8
V 16
to vacuum
PRV 2
V 7
V 17
V 18
DRAIN
PI 5
TI 2
SLURRY PUMP
PRV 4
VENT
V 5
V 6
PI 2
FREEZER
V 21
DRAIN
COOLING FANS
V 23
V 4
V 20
TI 3
SECONDARY COMPRESSOR
V 3
PI 6
V 26
DRAIN
V 24
TI 5
PI 8
PRIMARY COMPRESSOR
REFRIGERANT RECEIVER
TI 1
V 2
PRV 1
PI 1
V 19
REFRIGERANT PUMP
TI 4
PI 7
V 23
V 25
V 28
TO TEMPORARY FREON
V 1
V 29
to vacuum pump
FREON IN
V 22

Purification by froth flotation

ir. C. Mosmans

The purpose of this paper is to describe froth flotation and the guiding principles in the field of purification of contaminated soil and waste.

Purification by froth flotation.

The mosmans method has been used for the decontamination of soil and waste in the Netherlands since 1983. This method is effected by well chosen mineral seperation techniques which together result in a complete purification process. The most important, but also the most complex part of the mosmans method is the froth flotation technique.

Mosmans Mineraaltechniek BV is an independent organisation with a laboratory for research and development of mineral seperation methods. The laboratory spent several years to develop flotation processes for the purification of polluted soils, waste and waste effluents. It is fully equipped to carry out tests on batches from grammes to many tons by such processes as sampling, grinding, screening, classification, gravity concentration, dense media separation and several flotation methods.

As an extension of the laboratory efforts and to obtain real field experience and well trained operators a small processing plant has been in operation in the past six years. After several years of laboratory testwork the plant started in 1983 with the froth flotation of 10,000 tons of sandy soil. After that about 3,000 tons of copper containing muddy soil and 10,000 tons of earthy soil with lead.

A relatively difficult project was clayey soil from gasworks with complex cyanide and pca. For the very fine fraction (the slimes) special flotation techniques have been used.

This year a conspicious soil cleaning operation will be carried out in Zwitserland. This soil is contaminated with pesticides, herbicides and mercury during a fire in 1986.

Principles of froth flotation.

To achieve a separation between the contaminatives and soil in a soil-water mixture, the surfaces of the particles have to be adequately manipulated. In such a way that the former will be hydrophobic and the latter hydrophybic. The manipulation is not related to changing the chemical structure of the particles, but to modify the surfaces by selective adsorption. The hydrophobic particles glue themselves to air bubbles produced in the soil-water mixture.

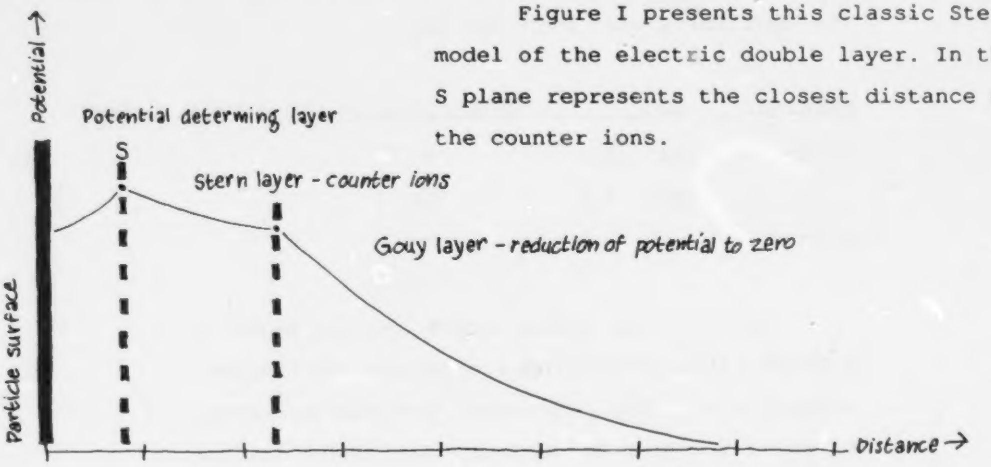
Flotation processes are determined by surface phenomina. The available surface depends on the grainsize. For example a cubic grain of mesh size of 1 cm covers an area of 6 cm2. By splitting this cube the total area increases.

Mesh size	total area	remarks
10,000 µm	6 cm^2	grains are too heavy for flotation
1,000 µm	60 cm^2	
100 µm	600 cm^2	normal froth flotation
10 µm	6,000 cm^2	
1 µm	60,000 cm^2	special flotation technology
0.1 µm	600,000 cm^2	

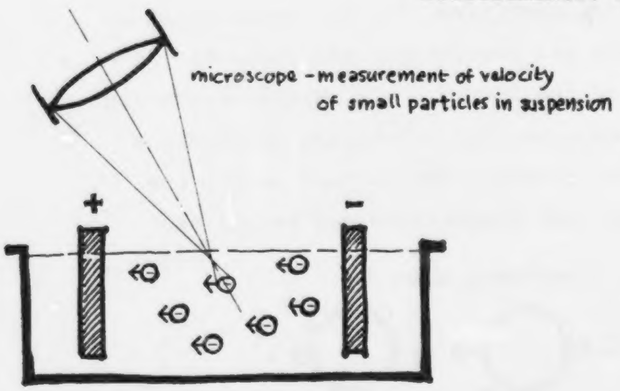
It is obvious that clay or silt has much more area/gramme than a sandy soil.

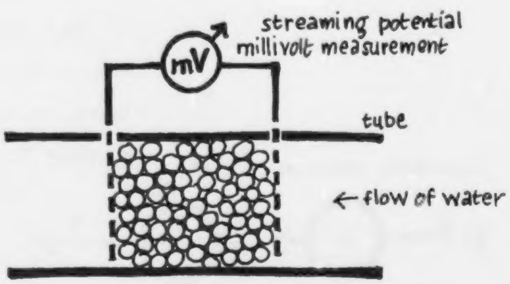
A particle in water obtains an electric surface charge due to partly ionisation, adsorption, orientation of dipoles or crystal lattice defects. Around the charged particle a diffuse layer or a cloud of counter ions with an opposite charge is formed, reducing the potential to zero. This phenomenon is called an electric double layer.

Figure I presents this classic Stern - Grahame model of the electric double layer. In the figure the S plane represents the closest distance of approach of the counter ions.



When the particles are forced to move in relation to the liquid, the slipping plane in the diffuse layer shows a potential, the Zeta potential. This electrokinetic phenomenon is very practical to study the manipulation of the surfaces. Two methods are in use, electrophoresis and streaming potential measurements. Figure 2 and 3 present these methods.


microscope - measurement of velocity of small particles in suspension
+
−
←⊖


streaming potential millivolt measurement
mV
tube
← flow of water

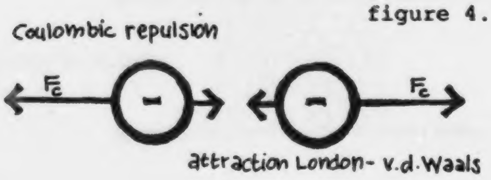
There are particular ions that are free to pass the electrical double layer. These ions are called potential determining ions. By a titration procedure the effect of these ions can be determinded. The condition which the ions compensate the surface charge is called zero point of charge or iso electric point. For example, for a particle $CaCO_3$ the potential determining ions are Ca, CO_3 and the pH, because of the equilibria with HCO_3 and CO_3.

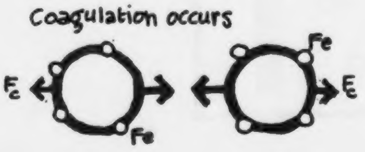
Material	ZPC	Controlled by the concentration
$CaCO_3$	pH 9,2	H
CaF_2	pCa 3,5	Ca
SiO_2	pH 2,5	H

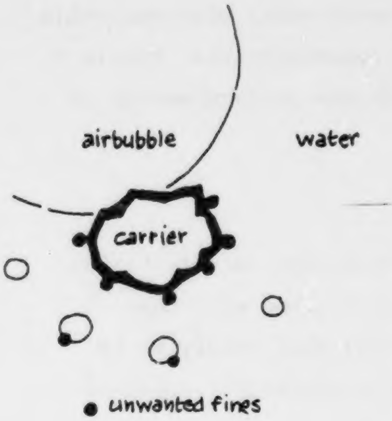
Counter ions which adsorb only by means of electrostatic attraction are called indifferent electrolytes. They "compress" the diffuse layer. Examples are Al-, Fe- and Ca-ions. These are the anorganic flocculants in water purification.

The third type of important ions exhibit surface activity and electrostatic attraction. They are called surface active counter ions. To these belong the wide range of flotation collectors,

The effects of an electrical double layer are illustrated by coagulation and a special flotation method for very fine particles. For the coagulation of two particles there are two forces, the coulombic repulsion force and the London - v.d. Waals attraction force, resulting in a barrier preventing coagulation. Addition of Fe-ions compress the diffuse layer, the barrier diminishes, and coagulation may occur, see figure 4.



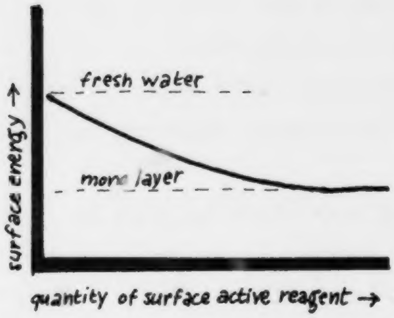




Fine contaminatives, say less than 5 µm are generally not floatable. But by the addition of coarse "carrier", particles and under conditions in which the unwanted fines adhere to the carrier, a purification by normal froth flotation of the carriers is possible, see figure 5.

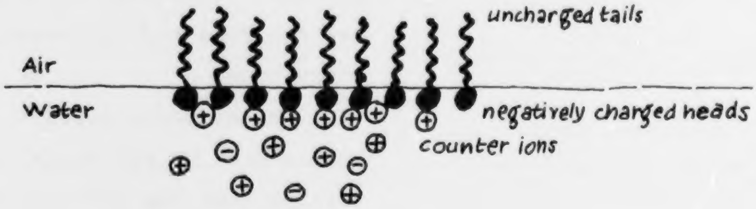
In froth flotation adhesion is necessary between the particles and the air bubbles rising through the pulp. There are three interfaces, particle - water, particle - air and water - air.

In fact, the thermodynamics of surfaces is valid for all the three interfaces. But for the sake of simplicity the particle - water interface is conform to the electrial double layer concept. The water - air interface is conform to the alteration of surface energy.



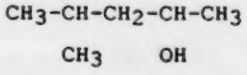
If a surface active or heteropolar reagent is added to water the surface energy decreases, see figure 6.

This is a result of the heteropolar nature of the compound. These molecules adsorp preferentially at the water-air interface. They are arranged with the hydrophobic tails into the air and the hydrophylic heads immersed into the water, see figure 7.



These surface active reagents are called frothers.

A few examples;



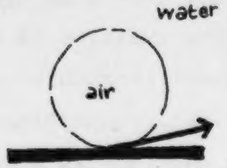
$$\underset{\displaystyle CH_3}{CH_3\text{-}CH}\text{-}CH_2\text{-}\underset{\displaystyle OH}{CH}\text{-}CH_3$$

methyl isobutyl carbinol

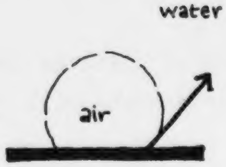
$CH_3\text{-}(O\text{-}C_3H_6)_n\text{-}OH$

polypropylene glycol

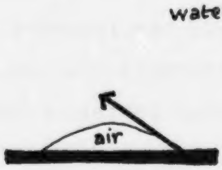
fig 8



particle A
"complete wettable"



particle B
"floatable"



particle C
"not wettable"

In the soil-water or waste-water mixture bubble contact must occur with the contaminatives. Figure 8 presents a cross section with the surface energy as surface tension (= ∂).

Investigations

The investigator has to manage many flotation variables. In addition he has to cope with the representativity of samples and with hardly to be determinated contaminatives. A consequent approach involves the following stages:

- Sampling of contaminated soil or waste.

The samples have to be representative, not only in respect to chemical but also in respect to mineralogical composition. If major differences exist between parts of the contaminated area, separate samples shall be obtained.
Sampling methods and sampling statistics as used in the mining industry are very useful.

- Determination of soil and contaminatives.

Chemical analysis provide only part of the information needed. Mineralogical analysis and grain size distribution are necessary for developing a flotation process. Techniques of mineralogical analysis are x-ray analysis and the examination by a petrographic microscope.

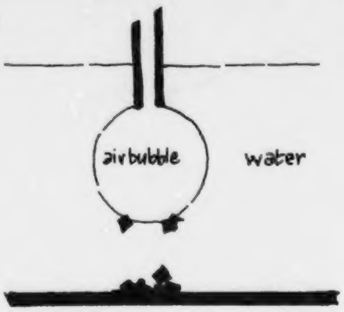
- Micro scale tests.

Bubble pick up technique, Hallimoand tube and air release tube are employed in flotation research of contaminated soils. Figure 9, 10 and 11, present these simple but effective and valuable methods.

- Batch testing

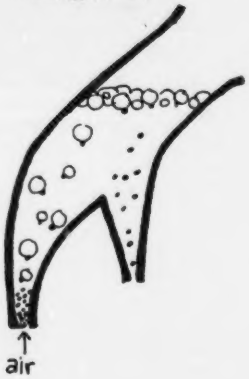
To investigate the flotation variables many tests with quantities of about half a kilogramme have to be carried out. Significant variables that are subject to bubble pick-up

fig 9



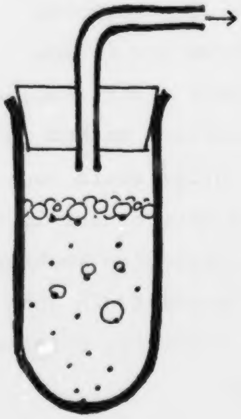
Hallimond tube

fig 10



vacuum flotation

fig 11



control are type of collector, frother, activator and depressor, pH, conditioning time, flotation time, pulp density and temperature.

In batch flotation a given mixture is fysico-chemically prepared, aerated, whereby it becomes separated into a froth and a residue.

The particles diminished into the froth according to:

$$C = Co\, e^{-St}$$

t = time
Co = concentrations at t = 0
S = constante (slope)

Figure 12 presents this idealized equation with data of sand, clay, water and complex cyanide. Each being expressed as a percentage of the initial quantity.

The research focuses on the alteration of slopes, to make them steeper for contaminatives and flatter for clay, silt, sand and (water).

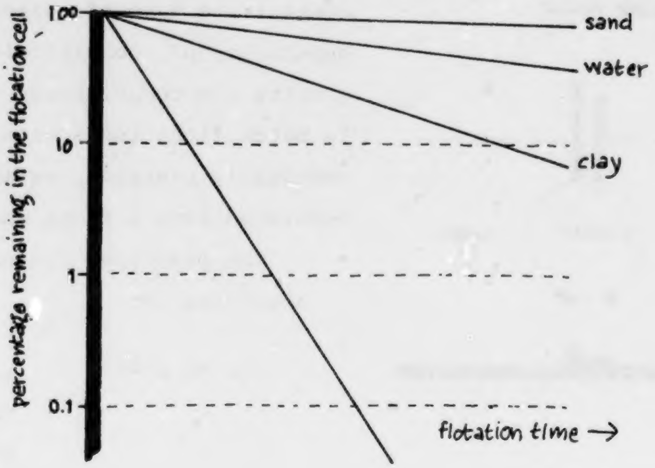
- Laboratory testing may be followed by pilot plant tests to provide continuous operating data for design, and to ensure that laboratory tests are reproducible on plant scale. Besides the possible build up of bicarbonates, sulphates, calcium and magnesium in the recirculating water should be studied. Flotation cells are arranged subsequently. Each cell separate only a part (the recovery) of the contaminatives.

For example, 50% recovery in each cell results for 4 cells in: 50% + 25% + 12,5% + 6,25% = 93.75% recovery.

- Plant practice in soil and waste flotation.

Each separation flow sheet represents the best solution at given conditions, such as volume of contaminated soil or waste, the desired final grade, data from laboratory work and available equipment.

fig 12



Note

The above mentioned mineral processing techniques have been adopted from the mining industrie. Over the past 75 years froth flotation has become the most important separation method in the mining industrie. Almost the entire world supply of copper, lead, zinc, nickel and many others is first collected in the froth of the flotation machine. But also nonmetallics are caught in the froth such as huge tonnages of phosphates, coal, fluorite, feldspar. soluble potassium chloride etc.

Reverse Osmosis: On-Site Treatability Study

Of

Landfill Leachate At The PAS Site In Oswego, NY

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Reverse Osmosis: On-Site Treatability Study
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1.0 Introduction

The Pollution Abatement Services (PAS) site in Oswego, New York, was remediated in the mid-1980's when drums of toxic wastes were removed from the site, and the contaminated soil was contained by means of traditional methods: a slurry wall along its perimeter, a leachate collection system, and a clay and high density polyethylene cap. The continuous monitoring and maintenance of this Superfund site has consisted of the collection and off-site treatment of approximately 65,000 gallons of leachate monthly. The leachate management methods has cost government agencies money, manpower and time. To reduce these expenditures, Region II of the United States Environmental Protection Agency (US EPA) requested the engineering assistance of the US EPA Environmental Response Team (ERT) to explore the feasibility of on-site treatment technologies.

In agreement with the 1986 Superfund Amendments Reauthorization Act (SARA), alternative and innovative technologies were preferentially addressed. Environmental engineers from the US EPA, Environment Canada, and the Response Engineering and Analytical Contractor (REAC) analyzed previous successful bench-scale work and selected reverse osmosis (RO) and enhanced ultraviolet oxidation, also called UV photolysis/ozonation/hydrogen peroxide, for a field pilot-scale study.

This paper concerns the application of reverse osmosis for on-site treatment of hazardous wastes. It reviews the basic principles that govern the process and reports on the treatability study that was conducted at the PAS site in the summer of 1988. Since four different brands of RO membranes were investigated, the evaluation of their performance focuses on the quality of their respective permeate. The purpose of this paper is to provide the preliminary results of this study.

2.0 Reverse Osmosis: The Treatment Technology

2.1 Process Description

Reverse osmosis (RO) is a membrane technology which can serve a dual-purpose in hazardous waste treatment. It is a means to reduce wastewater volumes, and in the process, the membrane generally retains most of the contamination within one of the two effluents, namely the concentrate. The permeate stream is aimed to be discharged in the environment, whereas the concentrate requires further treatment.

RO is accomplished by pumping an aqueous dilute solution at a high pressure over a semi-permeable membrane. As the solution sweeps the surface of the membrane, the solvent, water, is preferentially attracted. Its transport across the polymeric layer is driven by the difference between the osmotic pressure of the solution at that location on the membrane and the hydrostatic pressure of the solution.

The chemical substances present in a given feed solution differ in their affinity for the membrane material. The interaction between the membrane, the solute components, and the solvent governs the performance of any such system. Different schools of thought have explained the mechanism by which solutes are transported across the membrane. The most prevalent theories are : the preferential sorption-capillary flow mechanism (Sourirajan and Matsuura, 1985) and the solution-diffusion transport mechanism (Lonsdale et al. 1965).

Once the initial separation has been performed, the solution retained at the membrane surface is subjected to further separation as it flows along the polymeric surface. Thus, there is not only a step-wise change in solute concentration between the two sides of the membrane but also a gradual increase from the feed influent end to the concentrate effluent end on the same side of the membrane.

2.2 Applications

Reverse osmosis has been used extensively for the past twenty-five years to remove inorganic compounds for the production of potable water from brackish water and seawater. Economic and environmental considerations have promoted its use for concentrating electroplating rinse waters since the '70s, and its use has been explored for other hazardous waste treatment since then. Beginning in 1984, Environment Canada has been demonstrating reverse osmosis in the field for treating dilute organic solutions such as landfill leachate, industrial wastewater, and contaminated aqueous solutions generated by chemical spills. Some of the solutions successfully investigated in Canada include:

- ◊ spilled wood protection solutions containing tetra and pentachlorophenols (PCPs);
- ◊ leachate contaminated by volatile organic compounds;
- ◊ leachate contaminated by polychlorinated biphenyls (PCBs);
- ◊ potato wash water;
- ◊ fish blood water;
- ◊ pesticide container wash water;
- ◊ industrial wastewaters containing monoethylene glycol;
- ◊ surface runoff contaminated by benzene, toluene, and xylenes (BTX);
- ◊ solvent contaminated wastewater from an aircraft maintenance facility.

2.3 Pollutant Concentration Considerations

The influent pollutant concentration for which a reverse osmosis system will economically produce a permeate of sufficient quality for discharge in a sewer system or into surface waters varies from one chemical compound to another, and from one application to another. For example, a treatability study of an industrial waste effluent revealed that a reverse osmosis membrane would not withstand long-term exposure to a 1% phenol solution. However, selection of another membrane and a change in the chemical nature of the phenol allows the RO system to increase the phenol concentration up to 8% without either affecting the physico-chemical or the structural integrity of the RO membrane. As the permeate from the first stage is, at 1500 ppm phenol concentration, still too highly contaminated, a second stage has been added and the permeate meets the effluent discharge criteria set by the concerned jurisdiction. The phenol recovered by the two-stage RO system is expected to pay for the pollution control system within twelve months.

In this section, a review will be made of the two characteristics that play the most significant roles in defining the ranges of pollutant concentrations in which RO will be effective. These are the osmostic pressure and the chemical compatibility between the pollutants and the membrane materials.

2.3.1 Osmotic Pressure

Osmosis is a natural phenomenon. The term defines the diffusion of a solvent through a semi-permeable membrane which separates two solutions having different molar concentrations of solute. The semi-permeability of the membrane refers to this property to allow the solvent through but not the solute. An equilibrium is reached when the solvent flow stops. At this point, the hydrostatic pressure difference between the two liquid columns represents the osmotic pressure difference between the two solutions. To generate a net water transport through the membrane, the osmotic pressure difference must be overcome (Figure 1).

The osmotic pressure of an aqueous solution is caused by the presence of chemical species other than water. The type of compound and its concentration, the pH, and the temperature of the solution have an influence on the osmotic pressure, and thus, on the driving pressure necessary to induce reverse osmosis. The wastewater should exert an osmotic pressure no greater than the membrane's operating pressure limit to allow for water permeation.

2.3.2 Compatibility With Membrane Materials

The choice of a membrane is governed to a great extent by its chemical resistance. The membrane surface material, the backing polymer, the adhesive agents, the seals, and all related hardware must sustain the chemical abuse to which the pollutants might subject them. Reverse osmosis systems are mostly sensitive to long-term exposure to oxidants, and to low molecular weight halogenated organic solvents. Also, field experience reveals that some RO membranes tend to swell from long-term contact with BTX.

Membrane research and development continuously evolves as a result of customer demands, the introduction of new synthetic materials, and the quest for better performing membranes. Chemical resistance is constantly increased, in particular that to free chlorine, and the allowable feed pH range has been widened.

Finally, compatibility includes the notion that any pollutant will be rejected. It is undesirable that a membrane preferentially allows the permeation of contaminants.

2.4 Performance

In hazardous waste treatment, the ideal reverse osmosis membrane is one which: retains all pollutants; possesses a very high water permeation rate; chemically resists virtually all compounds; and needs very little maintenance (washing or replacement). However, RO membranes do not separate 100% of the contaminants and cannot recover 100% of the water from the contaminated solution. Thus, performance assessment of RO membranes is primarily based on the qualitative (percent rejection) and quantitative (water permeation) aspects of the separation.

2.4.1 Qualitative Aspects

Qualitative membrane performance is assessed by measuring the concentration of given solutes in the feed solution and in the permeate stream. From this data, the percent rejection is calculated by means of the following formula:

$$R_i = \left(1 - C_{ip} / C_{if} \right) \times 100\%$$

where: R_i is the rejection of solute "i" expressed as a percentage;
C_{ip} represents the concentration of solute "i" in the permeate;
C_{if} represents the concentration of solute "i" in the feed solution.

Rejection is considered from the perspective that a given solute is prevented from entering the permeate stream by the semipermeable membrane. In this sense, one should not confuse it with the removal of a given solute from the permeate.

Typically, a membrane retained for its rejection capability will cause a change in the pollutant concentration by one order of magnitude or more (in other words, a 90% rejection or more). As a result, the concentration of each pollutant in the feed greatly affects the number of stages needed to meet the effluent discharge criteria for the permeate.

2.4.2 Quantitative Aspects

RO systems are amenable to modular design. This characteristic allows for the manufacturing of systems to serve specific purposes, and yet, the productivity of each system can be increased by adding membrane modules, or replacing membranes within each module by better, and newly developed membranes, or by plumbing a second system to the first one.

All designs are based on the permeation rate of membranes. As each aqueous solution interacts differently with a given membrane, a systematic approach to determine the best membrane for each application must address the following aspects: the osmotic pressure expected and the necessity of special cleaning methods. In addition, the chemical compatibility of all materials should be examined.

Water recovery ratio is another quantitative criterion which is particularly important for wastewater volume reduction applications. It is defined as the portion of the feed solution which is recovered as permeate, and it conveniently corresponds to the volume reduction achieved. The ratio of the permeate flowrate to the sum of the concentrate and the permeate flowrates represents this quantity:

$$\Delta = Q_p / (Q_p + Q_c)$$

where: Δ is the water recovery ratio (expressed in percent or as a fraction);
Q_p is the permeate flowrate;
Q_c is the concentrate flowrate (units consistent to those used for Q_p).

Water recovery is limited by the rise in osmotic pressure that accompanies a volume reduction, and the precipitation of salts at the surface of the membrane. Therefore, a compromise must be reached between how much permeate should be recovered and the membrane maintenance needed to keep the membrane permeating.

2.4.3 Mass Rejection Rate

The mass rejection rate is a practical means to compare membranes. Its concept embraces the needs for high permeation rates, and for high contaminant rejections. Its calculation is performed by multiplying the permeate flowrate by the concentration difference existing between the feedwater and the permeate for a given contaminant. It represents the mass of a given contaminant which is prevented from entering the permeate or reciprocally that which is retained within the concentrate. A mass balance performed around a membrane system yields:

$$m_i = (C_{if} - C_{ip}) \bullet Q_p = (C_{ic} - C_{if}) \bullet Q_c$$

where: m_i is the mass rejection rate of solute "i";

C_{ic} is the concentration of solute "i" in the concentrate;

all other quantities, C_{if}, C_{ip}, Q_p, and Q_c were defined above.

2.5 Limitations To Reverse Osmosis

The following aspects may cause interferences to the RO membrane's performance: the feedwater source, the chemical compatibility of the membrane with respect to the feedwater composition, the solution osmotic pressure, fouling factors and scaling agents. Silt or colloids can become entrapped and significantly reduce productivity and rejection. The fouling potential is especially high for levels of iron higher than 0.1 ppm as the divalent form (Fe^{++}) will likely form colloidal iron (Fe^{+++}) in the presence of oxygen. Those salts which are most susceptible to precipitate as a scale on the membrane surface are calcium carbonate (limestone), calcium sulfate (gypsum), and silica. Hence, pretreatment should be addressed carefully as it will impact on the longevity of the RO membranes.

Various protective, monitoring and control components must be integrated to allow for the safe and reliable field operation of any reverse osmosis system. On the upstream end of the membranes, also called the feed end, filters act as a preventive measure by removing suspended solids down to the micronic size range. Generally it is recommended that particles having a size greater than one fifth of the smallest dimension of the feed conveying channel be removed. As a rule of thumb, 5 µm filters represents a suitable size for reverse osmosis (Lombard, 1986). In addition, pressure and temperature gauges and switches are normally incorporated. These ensure that the membranes will be used under normal operating conditions.

Currently, automation has yet to be developed to allow for feedback regulation of key operation parameters such as pressure, temperature, recirculation rate, and conductivity in the permeate.

3.0 Methodology

3.1 Leachate Characterization

Leachate characterization was carried out in December 1987. Samples collected at the PAS site in Oswego, NY , were analyzed by REAC. The analyses focused on: the total priority pollutants; total and suspended solids; titration curves; pH; TOC; BOD; COD; and flashpoint. The TOC level was 870 mg/l. Furthermore, the volatile organic compounds with the highest concentrations were: methylene chloride (25900 µg/l); trans-1,2-dichloroethene (13300 µg/l); xylenes (10000 µg/l total); toluene (6300 µg/l); and ethylbenzene (4100 µg/l). Also, analyses showed phenol (935 µg/l) and 2,4-dimethylphenol (435 µg/l) as the primary base/neutral/acid extractable compounds. No organochlorinated pesticide, nor polychlorinated biphenyl (PCB) was detected. Among all investigated metals, nickel (2150 µg/l), arsenic (35.3 µg/l), chromium (22.8 µg/l), and cadmium (16.0 µg/l) displayed the highest concentrations.

3.2 Bench Scale Treatability Study

As a result of the leachate characterization, phase I engineering studies were undertaken. Another sampling effort was performed at the PAS site on 23 February, 1988. It involved the complete filling of two 55-gallon lined drums (to eliminate headspace) and overpacking in 85-gallon drums. Subsequently, bench-scale testing was conducted at the River Road Environmental Technology Centre in Ottawa, Ontario, CANADA. Two leachate treatment schemes were investigated from 24 to 27 February, 1988. They were: powdered activated carbon adsorption followed by microfiltration (PAC-MF) and reverse osmosis; and two-pass reverse osmosis.

In both treatment tests, the landfill leachate was mildly acidified by hydrochloric acid addition to pH 6. As the rate of oxidation by oxygen is inversely proportional to the hydronium ion concentration, lowering the pH is meant to preserve iron as a ferrous salt solution, thereby preventing colloidal fouling of the membrane. The use of 5 µm filters provided additional protection against debris and particulate clogging. Analyses for the bench-scale studies covered: total priority pollutants plus 40 other pollutants except PCBs and pesticides; iron, calcium, and priority pollutant metals, sulfate; cyanide; total suspended and dissolved solids; TOC; and COD.

The rejection percentages of first pass RO alone, without PAC-MF, were respectively: 60.0% for methylene chloride; 78.4% for trans-1,2-dichloroethene; above 99.9% for xylenes (total); 98.9% for toluene; above 99.9% for ethyl benzene; and above 99.9% for benzene. For the semi-volatile organics phenol was rejected at 79.8% whereas higher results were exhibited for 2,4-dimethylphenol at 96.8%. In the case of inorganics, nickel (98.1%), arsenic (above 99.9%), lead (above 99.9%), and chromium (above 99.9%) were easily removed by reverse osmosis. TOC level was reduced by 88.8%. Second pass permeate did not significantly increase rejections over the first pass permeate levels.

The success achieved in this evaluation demonstrated reverse osmosis to be a technically feasible treatment for the PAS site. Also, potential savings identified in a subsequent economic analysis substantiated the need to proceed with the phase II engineering studies (Evangelista, 1988). On the other hand, powdered activated carbon adsorption followed by microfiltration separation appeared to be an unnecessary treatment step because of the economics and the generation of additional solid wastes.

3.3 Reverse Osmosis System Configuration For The On-Site Tests

The raw leachate was pretreated to lower the concentrations of the ferrous ion, and calcium carbonate, and solubilize residual metallic species. The following describes the pretreatment system. Batches of raw leachate were pumped from the recovery wells and piped to a concrete in-ground storage tank with a capacity of 200,000 litres. A stainless steel submersible pump fed raw leachate to the pretreatment system. The RO pretreatment steps included: basification; clarification; dead-end filtration; acidification and dead-end filtration. Basification included the injection of a 25% sodium hydroxide aqueous solution into the raw leachate stream within an on-line static mixer. Then, the basified leachate discharged into an 800-litre reaction tank. The flocculating solution was transferred to a Lamella® clarifier. The clarified effluent was then pumped through 5-micron and 0.2-micron cartridge filters in series, acidified by means of a 50% hydrochloric acid on-line injection, statically mixed, and finally discharged into a 2000-litre feed tank (Figure 2). Flows and pH were monitored and adjusted as to maintain a pH of 10 in the reaction tank, and a pH of 5 in the RO feed tank. The acidified leachate was then filtered through a 0.2-micron cartridge filter and introduced to two high pressure pumps before contacting the RO membranes for separation.

Environment Canada's mobile RO system was used for the phase II engineering studies. Its configuration was arranged to two pairs of 4"x40" spiral-wound membranes in series in each bank. Four different manufacturers' membranes were utilized in the course of this evaluation; therefore, each pair of RO membranes was representative of one brand.

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Tests were carried out over a period of 10 days in August, and September 1988. The distinction between each trial was established by a variation in the water recovery ratio, and in the operating pressure. Sufficient time was allowed between each sampling effort for the membranes' acclimatization.

Membrane separation generated concentrate and permeate effluents. The permeate could, at any point in time, be discretized into four separate streams for sampling purposes, each one being the product of one membrane type. The effluents were either directed to the enhanced ultraviolet oxidation system for further treatment or returned to an injection well in the landfill.

3.4 Sampling And Analysis Of Samples

Samples were taken at appropriate times during the trials from the RO feed solution, also called basified/acidified leachate, from each of the four permeate ports, and from the concentrate. The Lamella® clarifier sludge, and the raw leachate were each sampled on one occasion. REAC Standard Operating Procedures (SOPs) #2001 to 2005 were observed for sampling, sample storage, and sample shipment. All abovementioned SOPs are approved by the ERT (Evangelista, 1989). On-site analyses were performed for volatile organic compounds (VOCs) as per US EPA methods 601 and 602 using a Hewlett Packard (HP) 7675A purge and trap unit followed by a HP 5830 gas chromatograph (GC) with a flame ionization detector.

VOC analyses were verified off-site for some samples by a modified version of US EPA method 524.2 using a HP 5995C gas chromatograph/mass spectrophotometer (GC/MS) equipped with a Tekmar LSC 2000 purge and trap concentrator. The use of a reduced sample size, that is 5 ml, corresponded to the only adaptation to the analytical method of US EPA method 524.2 (Evangelista, 1989).

Off-site analyses were performed for the semi-volatile organics, also known as base neutral/acid extractables (BNAs), and priority pollutant metals. BNA analyses were done in conformity with the separator extraction technique of US EPA method 625 by means of a HP 5995C GC/MS. Finally, priority pollutant metals were analyzed according to the US EPA method 7000 series. Zinc and nickel were quantified by flame atomic absorption spectrophotometry using a Varian SpectrAA-300. In the case of arsenic and lead, graphite furnace atomic absorption spectrophotometry was performed using either a Varian 400-Z or a Varian SpectrAA-20 both set up with a GTA-95 graphite furnace unit (Evangelista, 1989).

4.0 Results and Discussion

For each test, the percent rejection of each membrane was computed for each pollutant. Then, the mean rejection was computed from the results of all tests. Table 1 lists those latter values for each of the four membranes labelled A to D. The selected pollutants were chosen because they represent various families of contaminants and because of their relative occurrence in the PAS site leachate. Therefore, the results tabled herein represent only a portion of those generated during the phase II engineering studies at the PAS site. However, the selection of representative pollutants is meant to provide a broad coverage of the quantification process. All the data can be found elsewhere (Evangelista, 1989).

In general, the RO membranes tested in this study rejected the heavy metals with the highest success. Among the organic compounds, the base/neutral/acid extractable compounds were more easily rejected than the VOCs. Membrane A rejected volatile organic compounds and semi-volatile organics at levels that did not reach 85% in most cases. The only exception was 2-methylnaphtalene (85.0%). A contaminant reduction of that order of magnitude was accomplished for all metals except for lead (10.3%) and zinc (45.4%). Membrane B tended to retain organic compounds at a higher percentage than membrane A. Among the VOCs, bromoform (91.5%), 1,1,1-trichloroethane (85.2%), and methyl isobutyl ketone (85.4%) were retained in the concentrate with the greatest rejection efficiency. The results for membrane B also revealed with more clarity than those for membrane A a trend of higher rejection levels with higher molecular weight. Benzoic acid (85.5%) and 1,2-dichlorobenzene (91.7%) were the BNAs which were separated with the greatest ease by membrane B. Rejections for metals exceeded the 85% level except for lead (16.9%) and zinc (33.[illegible]%). For membrane C, separation levels rarely exceeded 80%. The compounds that were separated above that percentage were: meta- and para-xylene (coeluted 84.6%); ortho-xylene (83.4%); 1,1,1-trichloroethane (85.7%); and copper (84.4%). Membrane D demonstrated its capacity to remove in excess of 90% of the contamination associated to six VOCs. These were: 1,1,1-trichloroethane (93.3%); bromodichloromethane (91.6%); bromoform (99.5%); ethylbenzene (94.9%); meta- and para-xylene (co-eluted 96.3%); and ortho-xylene (96.7%). Five compounds among the BNAs were separated at levels above 85%: 1,2 dichlorobenzene (87.9%); 4-methylphenol (89.8%); 2,4-dimethylphenol (88.5%); naphtalene (88.9%); 2-methylnaphtalene (92.6%). As for all membranes, removal of metals reached one order of magnitude except for lead (29.1%), and zinc (53.3%).

Overall, membrane D exhibited the best performance with the highest rejection levels for the majority of the contaminants. Of all membranes, membrane D achieved an order of magnitude change in the greatest number of pollutant concentrations.

The results indicate that the molecular size and polarity have an impact on the performance of RO membranes. The RO membrane rejects the larger molecules because the membrane acts as a molecular sieve. On the other hand, polar molecules are less amenable to separation than non-polar molecules. For example, benzene and toluene showed higher levels of rejection than the polar compounds phenol and 4-methylphenol. It is believed that the phenolics, when dissociated, can form a hydrogen bond with the membrane and diffuse through it more readily than a non-dissociated molecule.

To complete our analysis of the performance from a quantitative standpoint, the permeation rate of the single-stage RO system was examined for all twelve tests. Between 0 and 21.3 hours, six different tests were performed on separate days of operation where most of the fluctuations in the permeate flowrates are related to the start-up conditions, and the adjustment of the operating pressure (Figure 3). At 10.3 hours, the "spike" illustrates the effect of pressurizing the system from 600 psi to 800 psi. On the other hand, the increase in the combined permeate flowrate (12.5 to 27.0 litres per minute) that appears at 12.5 hours results from the use of a more dilute solution, namely the enhanced ultraviolet oxidation effluent. In the following tests, normal pretreatment of the leachate was resumed. The increase in the osmotic pressure that accompanied the change in the feed solution at 15.2 hours and a reduction of the operating pressure to 600 psi caused a decrease in the permeation rate from 28 to 22 lpm. This test ended at 19.5 hours. As the solutions left in the tanks lost during the following 20 hours of downtime part of their organic contamination through volatilization, the permeate rates reflected these losses at start-up. A pressure of 600 psi was maintained and flows gradually decreased to 10 litres per minute. This trial ended at 21.3 hours.

In the next sequence of tests, the variation in the permeate fluxes was mostly accounted by the adjustment of the water recovery ratio and the fluctuation in the chemical composition of the PAS site leachate. After 21.3 accumulated hours of operating time, tests were initiated at 800 psi, and the system was not shutdown until 63.8 hours. Varying the recovery ratio at a given pressure affected the permeation rate. When more water was recovered, the osmotic pressure increased at the membrane surface, therefore decreasing the permeation flux. On the other hand, different osmotic pressures of the feed were associated to different chemical compositions of the landfill leachate. At a fixed operating pressure and water recovery ratio, the changes in the osmotic pressure translated into a variable net driving pressure, and caused the instability in the permeate flowrates. The concentration ranges listed in Table 1 illustrate that for some chemical species, the concentration varied by as much as three orders of magnitude.

5.0 Conclusion

Rejection of metals is generally easily accomplished. Caution should be exercized when semi-volatile and volatile organic compounds are involved since the rejection efficiency is somewhat lower than for inorganic species. Still, acceptable levels of rejection can be achieved on some volatile organic compounds. For instance, membrane D rejected several volatile compounds at levels exceeding 90%. Therefore, membrane selection is an important step of any treatability study which is to involve reverse osmosis as a hazardous treatment process.

The preliminary results of the phase II engineering studies at the PAS site in Oswego, NY, demonstrated that reverse osmosis can be used as an effective part in a treatment process for landfill leachate. The economics of this separation process depends to a great extent on the liquid wastes themselves. The pretreatment of the feed water, the treatment/disposal of both the RO concentrate and the clarifier sludge bear heavily on the economics of the process. Discharge limits ultimately govern the costs and the benefits associated with this technology. The low rejections of volatile organics suggest that other treatment methods be coupled to a reverse osmosis system. Thus, RO should not be regarded as a panacea but as means to resolve specific contamination problems within the context of a treatment train where it can conveniently complement additional treatment processes.

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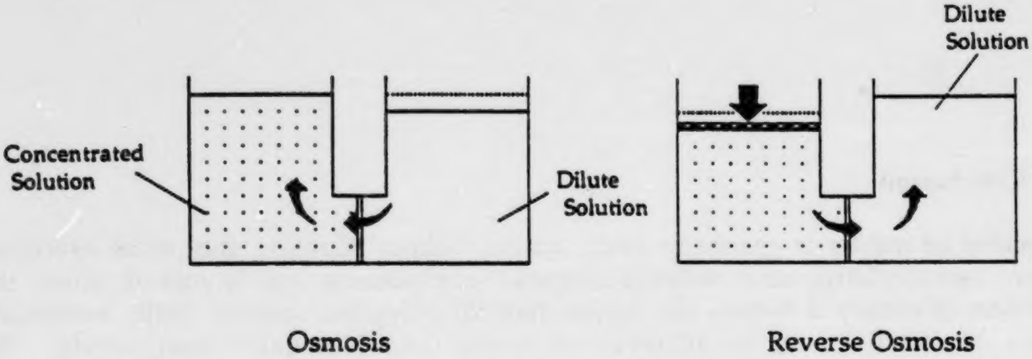
Concentrated Solution
Dilute Solution
Osmosis
Dilute Solution
Reverse Osmosis

Figure 1 - Osmosis: water transport through the semi-permeable membrane is from the dilute solution to the concentrated solution. At equilibrium, water flow stops, and the chemical potential is equal on both sides. The head difference is the osmotic pressure. Reverse osmosis: a pressure exceeding the osmotic pressure forces the water transport across the semi-permeable membrane. Solutes are for the most part retained on the side of the membrane where the pressure is applied.

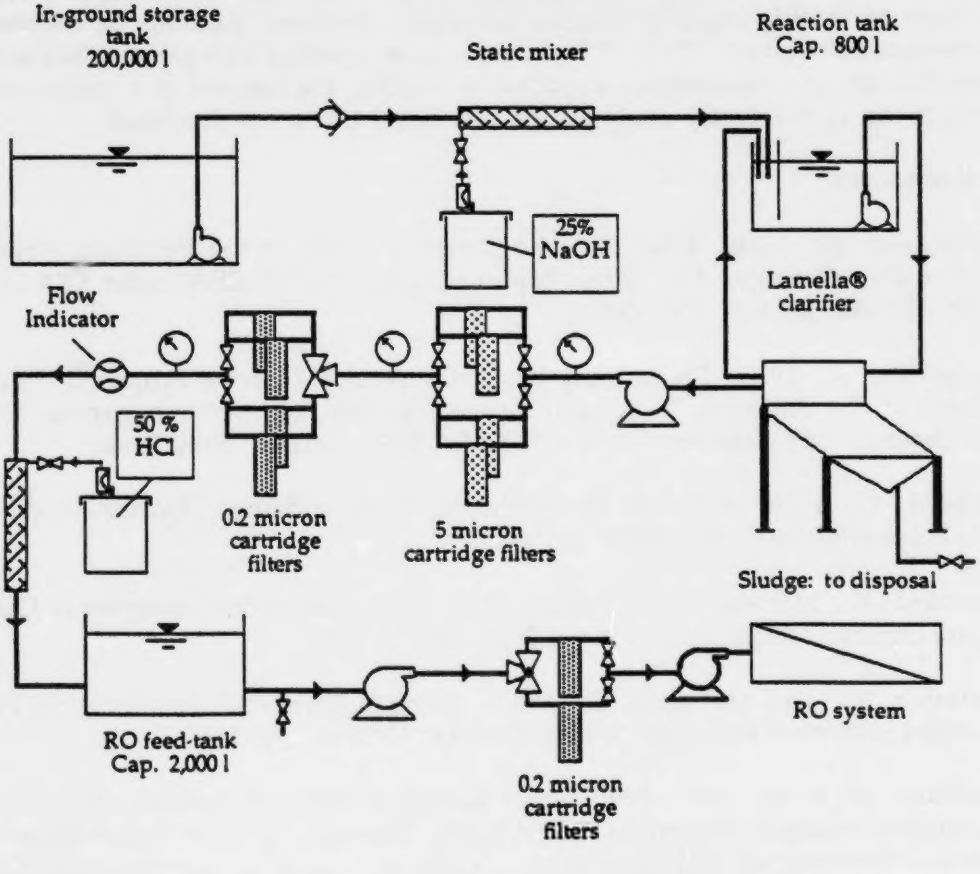
In-ground storage tank 200,000 l
Static mixer
Reaction tank Cap. 800 l
25% NaOH
Lamella® clarifier
Flow Indicator
50 % HCl
0.2 micron cartridge filters
5 micron cartridge filters
Sludge: to disposal
RO feed-tank Cap. 2,000 l
0.2 micron cartridge filters
RO system

Figure 2 - Pretreatment System Utilized for the Phase II Engineering Studies at the PAS Site in Oswego, NY.

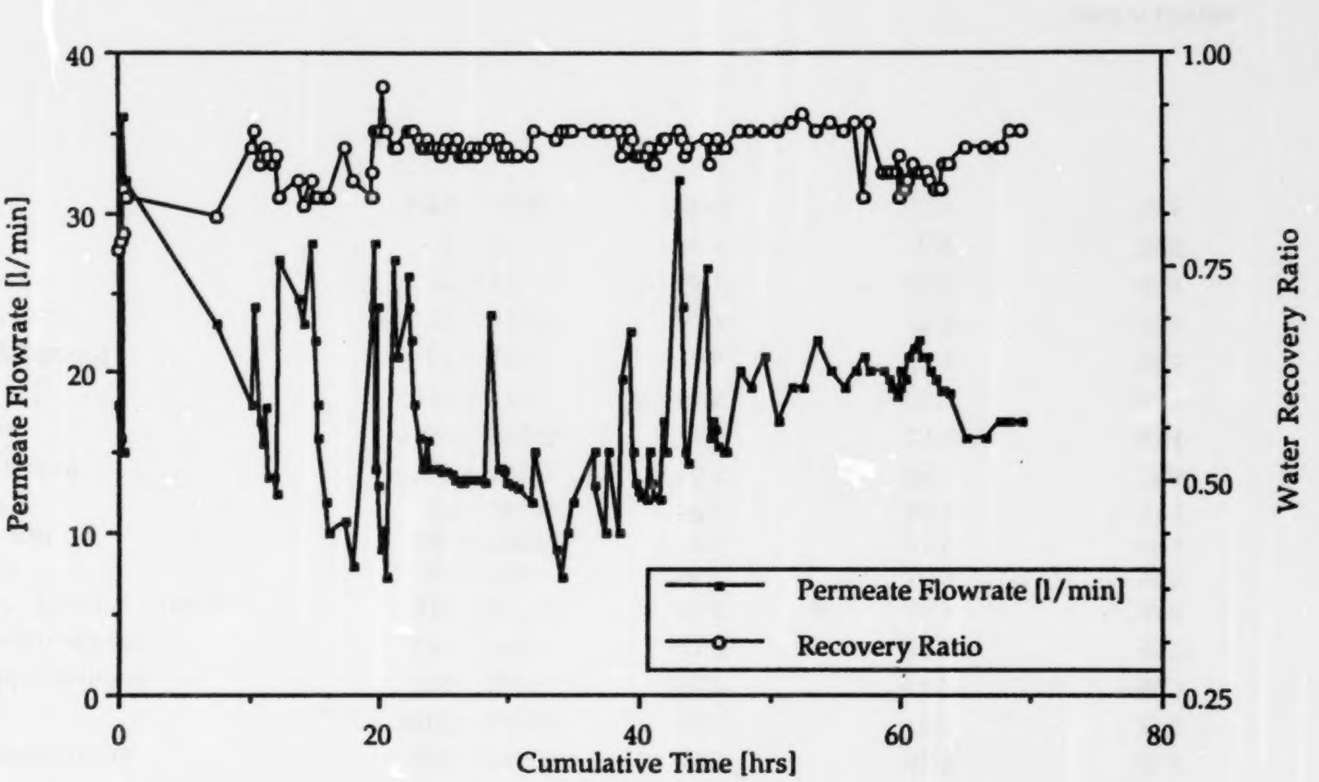

Figure 3 - Permeate Flowrate and Water Recovery During Phase II Engineering Studies at The PAS Site, Oswego, NY.

Table 1 - Summary of the Results
for the Phase II Engineering Studies at the PAS Site, Oswego, NY.

Compound/Metal	Concentration Range (in the feed) [µg/l]	Average Percent Rejection For All Tests Membrane A [%]	Membrane B [%]	Membrane C [%]	Membrane D [%]
Dichloromethane	129 - 99642	34.3	51.5	42.5	50.5
Acetone	4912 - 68768	46.0	49.5	31.6	73.8
1,1-Dichloroethane	178 - 3612	57.2	64.7	64.3	88.2
1,2-Dichloroethane	635 - 6931	41.0	52.3	53.7	75.3
trans-1,2- Dichloroethene	319 - 62577	11.7	37.3	37.0	47.4
Benzene	60 - 2561	56.7	58.0	55.8	83.9
Bromoform	226 - 198966	74.9	91.5	69.1	99.5
Toluene	75 - 26145	57.7	68.4	53.3	83.7
Ethylbenzene	1266 - 19211	66.1	74.3	74.6	94.9
o-Xylene	3339 - 52033	71.9	83.2	83.4	96.6
Phenol	121 - 7155	54.5	55.7	37.8	72.2
4-Methylphenol	67 - 4811	78.6	57.4	59.8	89.8
Benzoic Acid	46 - 42331	67.9	85.5	51.7	83.3
Arsenic	23 - 67	96.1	85.5	46.1	98.6
Lead	4 - 59	10.3	16.9	20.0	29.1
Nickel	1070 - 2630	>99.9	93.8	53.6	88.2

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KINETICS

Electro-Reclamation in theory and practice

ABSTRACT

During the last four years, Geokinetics has been developing a method to remove heavy metals and other contaminants from soil and groundwater. The method is based on the electrokinetical phenomena electro-osmosis, electrophoresis and electrolysis, which occur when the soil is electrically charged by means of one or several electrode-arrays.

The most important applications of these phenomena with respect to the soil have been the dewatering of clays by electro-osmosis and experiments to desalinize arable lands (USA, 1958 and USSR, 1966-1975). Experiments on a very small scale to remove heavy metals from soils are documented from UK (1980, 1981 and 1982). Though starting promisingly, the authors reported problems around the electrodes (precipitates), which influenced the process negatively.

Geokinetics has found a solution to these problems by developing an electrokinetical installation, which monitors and controls the chemical reaction environment around the electrodes. The core of such an installation consists of the electrode-series and their housing, which can be installed in principle at any depth, either horizontally or vertically. The housings are interconnected and form two separate (one for the cathode, one for the anode) circulation systems, filled with different chemical solutions. In these solutions the contaminants are captured and brought to a container-based water purification facility. The energy is supplied by a generating set or taken from the main.

Electro-Reclamation can be applied both in situ (soils) and on- or off site (excavated soil, scooped out river slush). The electrokinetical phenomena can also be used to fence off hazardous waste sites or potentially hazardous industrial sites.

The technique has been tested on the basis of numerous laboratory experiments, using different types of soil (clay, peat, argillaceous sand) and contaminants (As, Cd, Co, Cr, Cu, Hg, Ni, Mn, Mo, Pb, Sb, Zn). Besides, two in situ fieldexperiments (Cu, Pb and Zn) have been finished and one "official" in situ remediation project (As) has been succesfully terminated.

Reduction of individual heavy metal concentrations can be more than 90 %, depending on the energy supply and time duration.

Remediation costs are therefore directly related to these two factors. Costs range from less than US $ 50 per ton, when relatively low energy is supplied over long periods (several months), to more than US $ 400, when the time period is reduced to several weeks and the enrergy supply has to be increased accordingly. There is, however, a limit to the current strenght which can be used. In practice therefore an optimum is calculated for energy supply and time duration.

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Geokinetics

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Theory and Practice of Electro-Reclamation

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KINETICS

Electro-Reclamation in theory and practice

Electrokinetical phenomena

During the last 4 years Geokinetics has been developing a method to remove heavy metals and other contaminants from soil and groundwater. The method is based on electrokinetical phenomena, which in one way or another have been made use of since the end of the last century. These phenomena occur when the soil is electrically charged with DC by means of one or several electrode arrays :

1. **Electro-osmosis** : Movement of soil moisture or groundwater from the anode to the kathode.
2. **Electrophoresis** : Movement of soil particles within the soil moisture or groundwater.
3. **Electrolysis** : Movement of ions and ioncomplexes within the soil moisture or groundwater.

Electro-osmosis

the electro-osmotic transport depends on the following factors :

- the mobility of the ions and charged particles within the soil moisture or groundwater;
- the hydratation of the ions and the charged particles;
- the charge and direction of the ions and charged particles, which cause a net water movement;
- the ion-concentration;
- the viscosity of the pore solution, depending a.o. on the capillary size;
- the dielectrical constant, depending a.o. on the amount of organic and anorganic particles in the pore solution;
- the temperature.

From existing literature and own experiments the average electro-osmotic mobility has been calculated to be in the order of 5.10^{-9} $m^2/U.s$, where U = potential drop (V/m).

To drain 1 m^3 of soil by electro-osmosis, the following parameters should be known :

- the porosity;
- the moisture content of the soil to be treated;
- the conductivity of the pore solution;

Apart from these other factors like the desired time period, the use of the soil after treatment and safety requirements regards maximum voltage and current are also of importance.

Electrophoresis

Electrophoresis (kataphoresis) is the process of movement of particles under the influence of an electrical field. With particles is meant all electrically charged particles like colloids, clay particles floating in the pore solution, organic particles, droplets etc.

The mobility of these particles corresponds with that of ions. Within the pore solution these particles transfer the electrical charges and affect the electrical conductivity and the electro-osmotic current. Clay minerals as such have 2 electrical polarity possibilities. One consists of the stucture-based dipole moment, which depends on the atomic masses and has an orientation parallel to the longest axis of the clay particle. The second polarity stands at right angles to the first and is caused by the external electrical field. It depends on the way of polarization of the electrical double layer. The mobility of clay particles is an interplay between these two moments and is, therfore, less than the electro-osmotic mobility. It varies between 1.10^{-10} and 3.10^{-9} $m^2/U.s$.

Electrolysis

Analogous to electro-osmosis and electrophoresis, where one considers only water transport or particle transport respectively, with electrolysis only the movement of ions and ioncomplexes is taken into consideration. The average mobility of ions lies around 5.10^{-8} $m^2/U.s$, which is a factor 10 greater than that of the electro-osmotic mobility. Therefore, the energy necessary to move all ions over an average distance of 1 m through a 1 m^2 soil section is 10 times less than with electro-osmosis.

To calculate the energy necessary to dispose of the contaminants within 1 m^3 of soil, the following factors are of importance :

- the chemical form of the contaminants;
- the concentration of the contaminants;
- the required concentrations of the contaminants;
- the behaviour of the contaminants at different pH-levels;
- pH-control around the electrodes within the soil;
- removal of the contaminants and particles at the respective electrodes;
- supply of a conditioning solution to replace the removed contaminants and other particles at the electrodes;
- processing of the contaminated solution removed at the electrodes.

The application of electrokinetical phenomena in practice

Up to a few years ago the most important application of electrokinetical phenomena with respect tot the soil had been the dewatering of clays by electro-osmosis. Apart from that experiments and research in the USA (Collopy, 1958) and the USSR (Vadyunina et al., 1966-1975) were aimed at developing a technique to remove accumulated salts from agricultural terrains.
Experiments on a very small scale both in the laboratory and in the field are documented by Hamnet (1980), Agard (1981) and Warfield (1982). These experiments were aimed at the removal of heavy metals from the soil. Though the experiments started promisingly, the authors reported problems around the electrodes (chemical precipitates) after a certain time period, which influenced the process in an adversative way. Especially the changing of the pH around both electrodes influences the mobility of the heavy (and also lighter) metals.

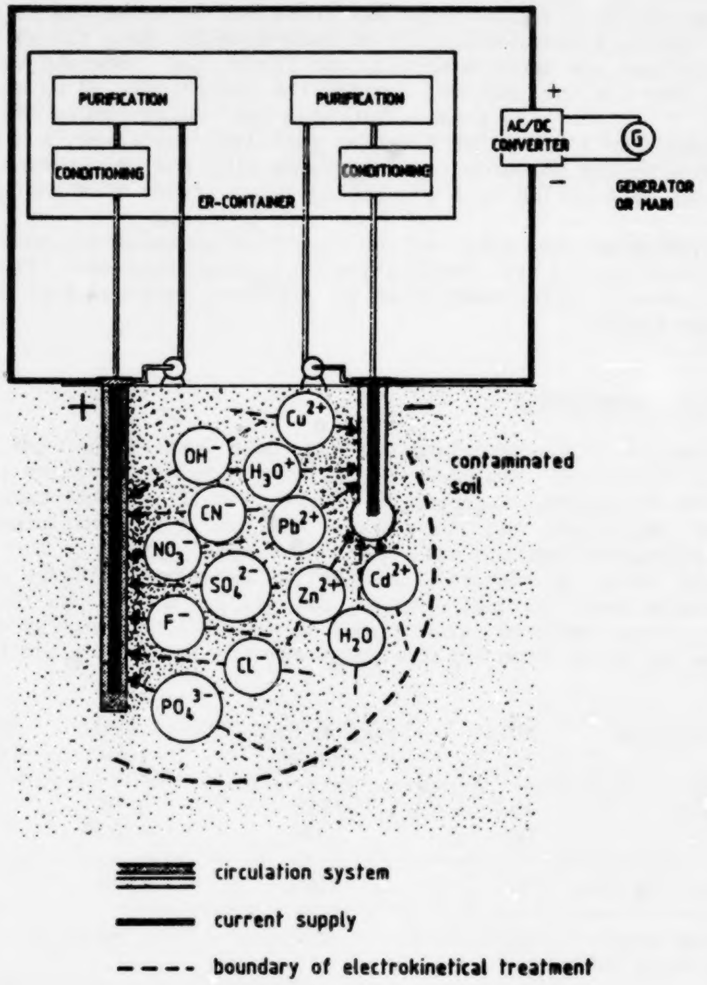

PURIFICATION
PURIFICATION
CONDITIONING
CONDITIONING
ER-CONTAINER
+
AC/DC CONVERTER
−
G
GENERATOR OR MAIN
+
−
Cu^{2+}
OH^-
H_3O^+
CN^-
Pb^{2+}
NO_3^-
SO_4^{2-}
Zn^{2+}
Cd^{2+}
F^-
H_2O
Cl^-
PO_4^{3-}
contaminated soil
circulation system
current supply
boundary of electrokinetical treatment

Fig. 1 : Schematic representation of ER-field unit and electrokinetical transport in the soil

Electrokinetical Installation

Geokinetics has found a solution to these problems. Both for the laboratory and the field an electrokinetical installation has been developed, which controls the chemical reaction environment around the electrodes. The electrokinetical processes are monitored and managed actively, thus averting adverse effects.

The core of an electrokinetical installation (fig. 1) consists of the electrode-series and their housing. These can be installed in principle at any depth, either vertically or horizontally. Both the cathode- and anode housings are interconnected and form two seperate circulation systems (one for the cathode, one for the anode), filled with different chemical solutions. In these solutions the contaminants are captured and brought to a water purification facility, installed in a container together with the solution tanks and measuring and monitoring devices. The energy is supplied by a generating-set or taken from the main.

The consequence of this set-up is, that electro-reclamation can be applied both for in situ remediation of contaminated soil (fig. 2) and for on- or off site remediation of excavated polluted soil or scooped out river slush.

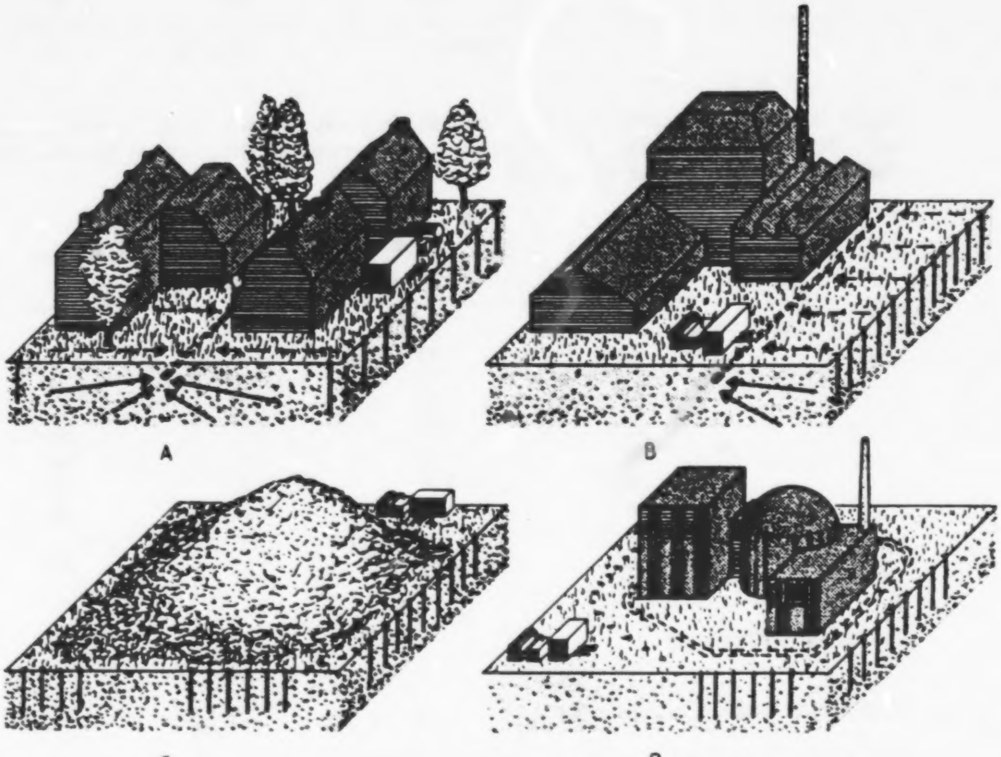
Laboratory experiments

The method of electro-reclamtion has been tested on the basis of numerous laboratory experiments. They focussed on important parameters like kind of current, strength of current, voltage, moisture content, chemical additives and the like. Besides, the effectiviness of the method as regards certain soil- and heavy-metal types has been examined with the help of several simulation experiments (clay, peat, fine argillaceous sand polluted with As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Zn). They rendered also a good insight into the energy demand and the time duration. Some results are presented in table 1 and figures 3a and 3b.

Soil type	Metal	Conc. before (ppm)	Conc. after (ppm)	Energy (kWh/ton)
Peat	Pb	9000	2400	56
	Cu	500	200	56
Pottery clay	Cu	1000	100	14
Fine argillaceous sand	Cd	275	40	110
Clay	As	300	30	115

Table 1.

The next table shows the results before and after treatment of a soil sample of fine argillaceous sand, contaminated with several metals. The energy demand amounted to 30 kWh/ton.



A) Remediation of residential areas
B) Remediation of industrial areas
C) Remediation/fencing of hazardous waste sites
D) Preventive electrokinetical fence around potentially hazardous industrial complexes

Fig. 2 : Some applications of in situ Electro-Reclamation

Soil type	Metal	Conc. before (ppm)	Conc. after (ppm)	Decrease (%)
Fine argillaceous sand	Cd	319	< 1	99
	Cr	221	20	91
	Ni	227	34	85
	Pb	638	230	64
	Hg	334	110	67
	Cu	570	50	91
	Zn	937	180	81
		Table 2.	Average :	83

Table 3 lists the results of a laboratory experiment with a sample of mud, dredged from the river Weser in Germany. The energy demand for this experiment amounted to 100 kWh/ton.

Soil type	Metal	Conc. before (ppm)	Conc. after (ppm)	Decrease (%)
River slush	Cd	10	5	50
	Cu	143	41	71
	Pb	173	80	54
	Ni	56	5	91
	Zn	901	54	94
	Cr	72	26	64
	Hg	0.5	0.2	60
	As	13	4.4	66
		Table 3.		69

Fieldexperiments

Fieldexperiment 1

The first fieldexperiment took place alongside part of a waterbearing ditch, on one side bordered by a former paint-factory and on the other side by open grassland. The bank on the latter part was heightened by sediment dredged from the ditch. This sediment was heavily polluted with metals in the form of paint residuary. The raised sediment layer, height 20 - 50 cm, length 70 m and width 3 m, contained Pb and Cu concentrations up to 10,000 ppm and 5,000 ppm respectively. The original peat soil underneath was contaminated by leaching of this overlying layer with Pb-concentrations ranging from 300 ppm to more than 5,000 ppm, while Cu-concentrations were in the order of 500 to 1,000 ppm.

A preceding laboratory test with a sample of the sediment reduced the concentration of Pb from ≈ 9,000 ppm to ≈ 5,000 ppm and that of Cu from ≈ 4,500 ppm to ≈ 1,600 ppm, all within a time period of 320 hours.
For the fieldexperiment one cathode- and one anode-series were installed both with a length of 70 m and a mutual distance of 3 m.

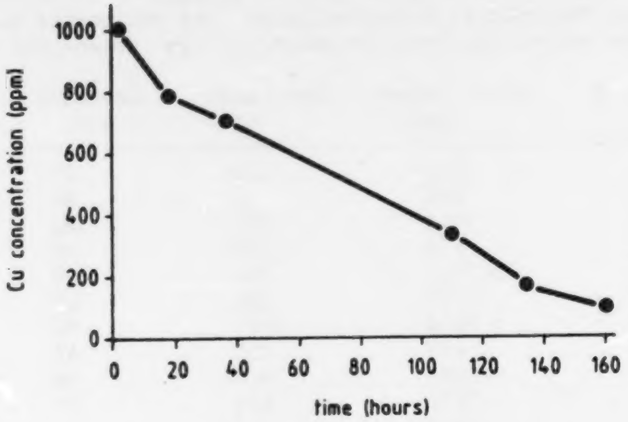


Fig. 3a : Decrease of Copper during electrokinetical treatment of contaminated pottery clay

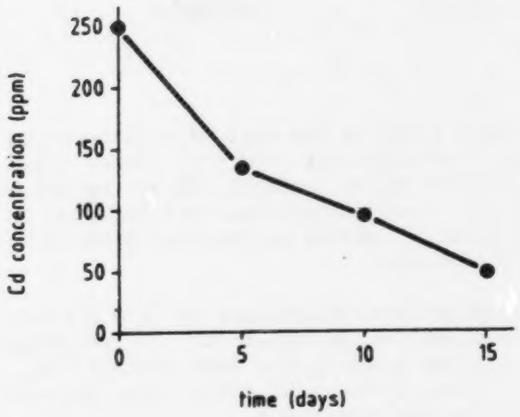


Fig. 3b : Decrease of Cadmium during electrokinetical treatment of contaminated fine argillaceous sand

The cathode was installed horizontally, while the anodes were implaced vertically into the soil about 2 m apart. On the basis of the energy consumption during the laboratory test the fieldexperiment was confined to 430 hours.
The changes in Pb- and Cu-concentrations were monitored at 26 sampling locations, sampled at regular intervals at several depths (10,20,30,40 and 50 cm below groundsurface). The following table lists part of the analysis-results for Cu and Pb within the peat at a depth of 30 to 40 cm below ground surface. The spatial distribution of the pollutants at the beginning and at the end of the test are shown in figs. 4a and 4b).

Sample point (30-40 cm b.gs)	Metal	Conc. before (ppm)	Conc. after (ppm)	Decrease (%)
1	Pb	440	110	75
1	Cu	185	35	81
2	Pb	3900	700	82
2	Cu	540	220	59
3	Pb	> 5000	560	89
3	Cu	1150	580	50
4	Pb	> 5000	2450	51
4	Cu	475	250	47
5	Pb	> 5000	610	88
5	Cu	1170	230	80
6	Pb	> 5000	300	94
6	Cu	580	45	92
7	Pb	3780	285	92
7	Cu	410	30	93
8	Pb	380	180	53
8	Cu	35	15	57
9	Pb	340	90	74
9	Cu	50	15	70
			Average :	74

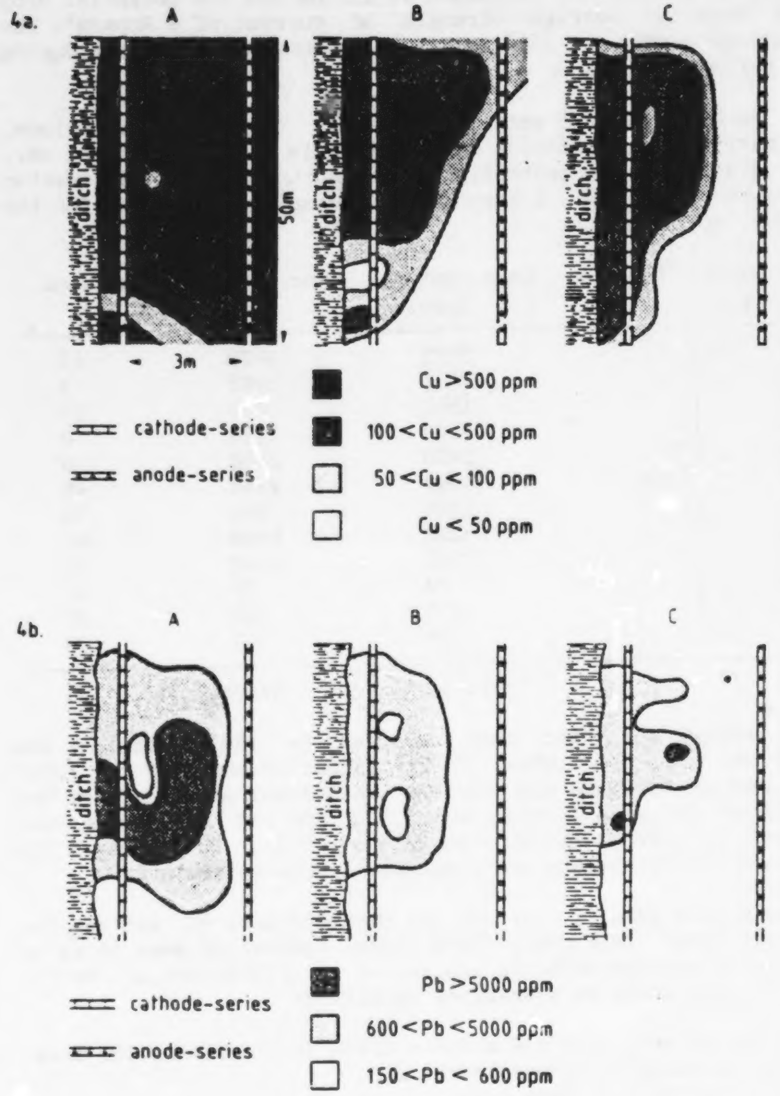
Table 4

Fieldexperiment 2

The second fieldexperiment was carried out on the site of a galvanizing plant. According to preceding investigations the soil (sandy clay) around the plant was contaminated with Zn to a depth of 40 cm below groundsurface. In the upper 10 cm Zn-concentrations were reported to have a maximum of 3,000 ppm. At greater depths Zn-concentrations were indicated as being in the order of 500 ppm.

For the experiment an area was selected with dimensions of 15 m x 6 m x 1 m. Two cathode-drains were installed at a depth of 50 cm below groundsurface, while 33 anodes, divided along 3 rows were implaced in holes of 1 m depth with a mutual distance of 1.5 m. The distance between the cathode- and anode-series was also 1.5 m.

Energy was supplied by a 100 kVA generating set. The resistivity of the soil was 5 Ωm. The installation was calculated for a DC-supply of 8 Amps/m^2 of soil, which should result in a potential drop of 40 V/m. This potential drop could not be maintained during the whole period. As a result of some material problems it was neither possible to maintain a 24 hour energy-supply to the soil.


4a.
A
B
C
ditch
ditch
ditch
50m
3m
cathode-series
anode-series
Cu >500 ppm
100< Cu <500 ppm
50< Cu < 100 ppm
Cu < 50 ppm
4b.
A
B
C
ditch
ditch
ditch
cathode-series
anode-series
Pb >5000 ppm
600< Pb <5000 ppm
150< Pb < 600 ppm

A) Sampling at 17-04-87
B) Sampling at 22-05-87
C) Sampling at 25-06-87

Fig. 4 Results of fieldtest 1
4a Decrease of Cu
4b Decrease of Pb

Within 2 weeks temperature rose from 12 °C to an average of 40 °C. As a consequence soil resistivity decreased to 2.5 Ωm and the potential drop to 20 V/m with an average strength of current of 8 Amps/m^2. The effective energy-supply per 1000 kg of soil amounted to 160 kWh during the 8 week period.

Changes in Zn-concentration were monitored at 12 sampling locations, which were sampled at 3 different depth intervals (10, 30 and 50 cm). Changes in groundwater concentration were monitored in 2 observation wells. In table 5 and fig. 5 the analysis-results are given for the depth interval of 30 cm.

Sample point (30 cm b.g.s.)	Metal	Conc. before (ppm)	Conc. after (ppm)	decrease (%)
1	Zn	5120	4470	13
2		2030	1960	3
3		1600	800	50
4		2320	2320	0
5		2450	2450	0
6		4390	2360	48
7		1960	940	52
8		3250	1960	40
9		2400	2000	17
10		70	30	57
11		150	120	20
12		120	80	33
			Average :	20

Table 5.

The energy demand for this test amounted to 160 kWh/ton. At the beginning of the test the highest Zn-concentration amounted to 7,010 ppm with an average of 2,410 ppm over the whole area. At the end of the test the highest Zn-concentration was 5,300 ppm and the average had been decreased to 1,620. The concentrations of Zn, Pb and Cd in the groundwater and the filtercake are presented in the tables 6 to 8.

A total of some 1000 kg of filtercake was produced with an average Zn-content of 117 g/kg. This comes to a total removal of some 50 kg of zinc, assuming an average moisture content of the filtercake of 60 % . A rough mass-balans could be summarized as follows :

- treated volume of soil : 15 x 6 x 0.5 x 3/4 = 34 m^3 (1/4 of the area did not show increased Zn-concentrations).
- Weight : 34 m^3 x 1.8 = 61 tons.
- Weight of filtercake : 1000 kg.
- average moisture content : 60 %
- total dry matter : 400 kg.
- average Zn-concentration : 117 g/kg.
- amount of zinc removed : 47 kg
- removed per 1000 kg of soil : $47 \times 10^6 / 61 \times 10^3$ = 770 ppm.

The last value is in the same order of magnitude as the average decrease in Zn-concentration (2410 ppm -1620 ppm = 790 ppm).

An important outcome of the test was the relatively high energy consumption against a rather low Zn-mobility. This was the result of the high buffering capacity of the soil, caused by the presence of NH_3 and NH_4Cl (as was established later), which is used during the galvanizing process. During a following laboratory test with a soil sample from the area it was found that the energy necessary to reduce Zn-concentrations below the 200 ppm level would amount to 500 kWh/ton of soil. With an unchanged power-suplly of 100 kVA this would mean tripling the time period of 8 weeks to 24 weeks.

Metal	:	Zn	Pb	Cd	Zn	Pb	Cd
sample treatment	:	not acidified			acidified		
date	obs. well	ppm					
24-10-88	1	200	0.09	0.06	270	1.4	0.07
01-11-88	1	120	0.07	0.00	140	0.09	0
09-11-88	1	130	0.06	0.02	160	0.17	0.02
17-11-88	1	172	0.07	0.03	198	0.11	0.04
25-11-88	1	130	0.17	0.03	180	0.22	0.03
30-11-88	1	120	0.13	0.03	150	0.16	0.03
24-10-88	2	10	0.17	0.02	40	0.34	0.02
01-11-88	2	1.5	0.09	0.09	2	0.15	0
09-11-88	2	2.5	0.06	0	3	0.15	0
17-11-88	2	6	0.03	0	8	0.07	0.01
25-11-88	2	2.8	0.03	0.01	5.8	0.18	0.01
30-11-88	2	4	0.09	0	5.5	0.14	0

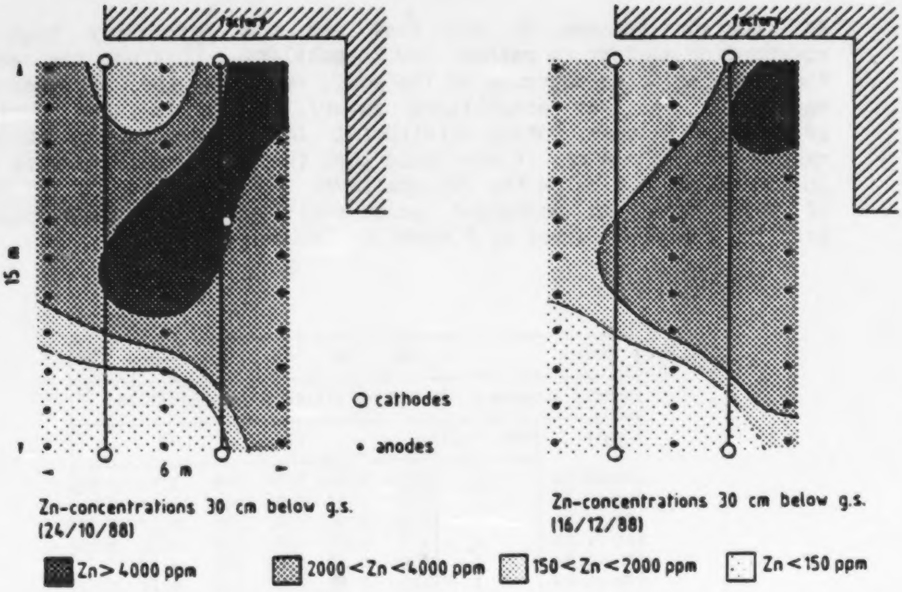
Table 6. Zn-content (ppm) of the groundwater in observation wells 1 and 2.

Metal :	Zn	Pb	Cd	moisture cnt
date	g/kg			in %
24-10-88	136.9	1.9	0.34	
09-11-88	199	1.1	0.18	
17-11-88	99	2	0.12	
25-11-88	89	1.5	0.16	78
30-11-88	61	0.58	0.11	

Table 7. Zn-content (g/kg) of the filtercake during Electro-Reclamation.

Metal :	Zn	Pb	Cd
date	ppm		
30-11-88	30	0.6	0

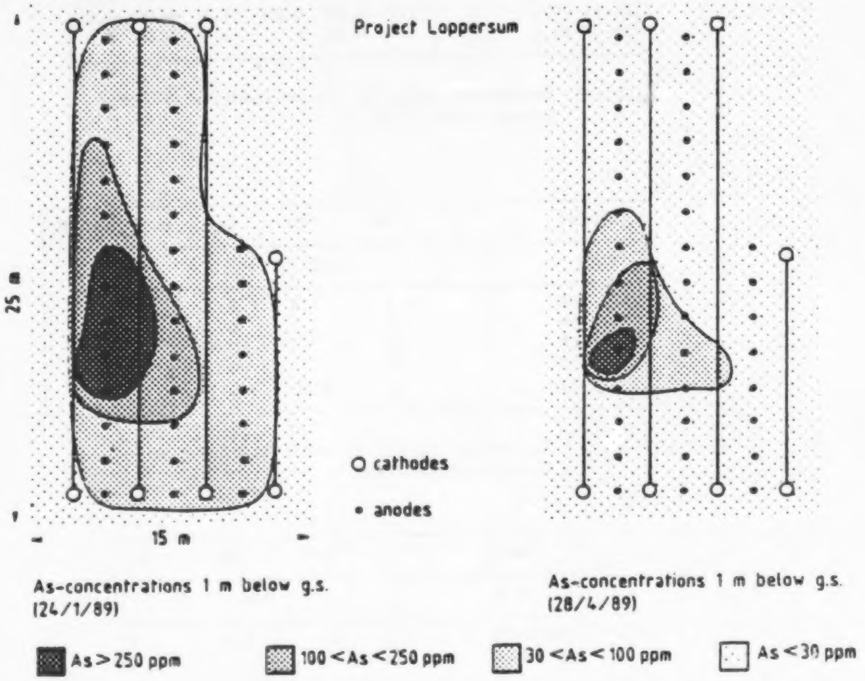
Table 8. Zn-content (ppm) of the solution in the anode-circulation system.


factory
factory
15 m
6 m
O cathodes
• anodes
Zn > 4000 ppm
2000 < Zn < 4000 ppm
150 < Zn < 2000 ppm
Zn < 150 ppm

Zn-concentrations 30 cm below g.s. (24/10/88)

Zn-concentrations 30 cm below g.s. (16/12/88)

Fig. 5 : Results of fieldtest 2


Project Loppersum
25 m
15 m
O cathodes
• anodes
As > 250 ppm
100 < As < 250 ppm
30 < As < 100 ppm
As < 30 ppm

As-concentrations 1 m below g.s. (24/1/89)

As-concentrations 1 m below g.s. (28/4/89)

Fig. 6 : Results of remedial action project 1

Remedial action Project 1

The first 'official' Electro-Reclamation project started at the end of January 1989. It concerned an As-pollution on the site of a former timber-impregnation plant. After a fire in 1984, which destroyed a large part of the plant, it was decided not to rebuild the plant. After dismantling the same a 'statement of unpolluted soil' was needed in order to allocate the land to building plots. A following investigation established the presence of As-concentrations up to several 100 ppm in part of the heavy clay soil to a maximum depth of 2 m. Cause of the pollution was attributed to 'Superwolmansalt D'($Na_2HAsO_4.7H_2O$), used for impregnation.

In April 1988 Geokinetics was requested to investigate the possibility of remediating the soil by Electro-Reclamation. A following laboratory test with a soil sample reduced the As-concentration of 300 ppm to 30 ppm against an energy consumption of 115 kWh/ton. An additional field investigation delineated the pollution to an area of 10 m x 10 m, contaminated to a depth of 2 m and an adjoining area of 10 m x 5 m, contaminated to a depth of 1 m. Total volume of polluted soil : 250 m^3 (= 450 tons).

The project started in January 1989. Along the length of the polluted area 4 x 2 cathode-drains were installed : one at a depth of 1.5 m and the other at 0.5 m. The cathode-series had a mutual distance of 3 m. In between 36 anodes were implaced in the soil, divided along 2 rows of 14 and 1 row of 8 pieces. Within the area of 10 m x 10 m the anodes were installed to a depth of 2 m below ground surface. In the other area of 10 m x 5 m the depth of the anodes was limited to 1 m depth. All anodes were placed at a mutual distance of 1.5 m.

On the basis of both the laboratory test and the field investigation the duration of the Electro-Reclamation period was calculated to last 50 (24 hour) days, using an energy-supply of 200 kVA (= 44 kW effective into the soil.

At the beginning the resistivity of the clay was 10 Ωm and soil temperature at a depth of 0.5 m was 7 °C. After 3 to 4 weeks temperature had risen to an average of 50 °C, while the resistivity decreased to 5 Ωm. The original potential drop of 40 V/m decreased accordingly to 20 V/m with an average current-strength of 4 Amps/m^2 (total crosssectional area being 110 m^2).

Changes in As-concentrations were monitored at 10 fixed sampling locations and numerous randomly distributed sampling-points. Of the fixed locations, 2 were sampled at 0, 0.5, 1, 1.5 and 2 m depth. The others at 0, 0.5 and 1 m depth. The analysis-results at a depth of 1 m below ground surface are listed in table 9 and fig. 6. The last sampling date being April 30th.

With an average As-concentration over the whole area of 110 ppm before the process started, the total As-content amounted to some 50 kg. On April 30, 3/4 of the area showed As-concentrations below the required 30 ppm boundary. One spot remained, however, with relatively high As-concentrations. Calaculations showed, that some 25 to 30 kg of arsenic had been removed.

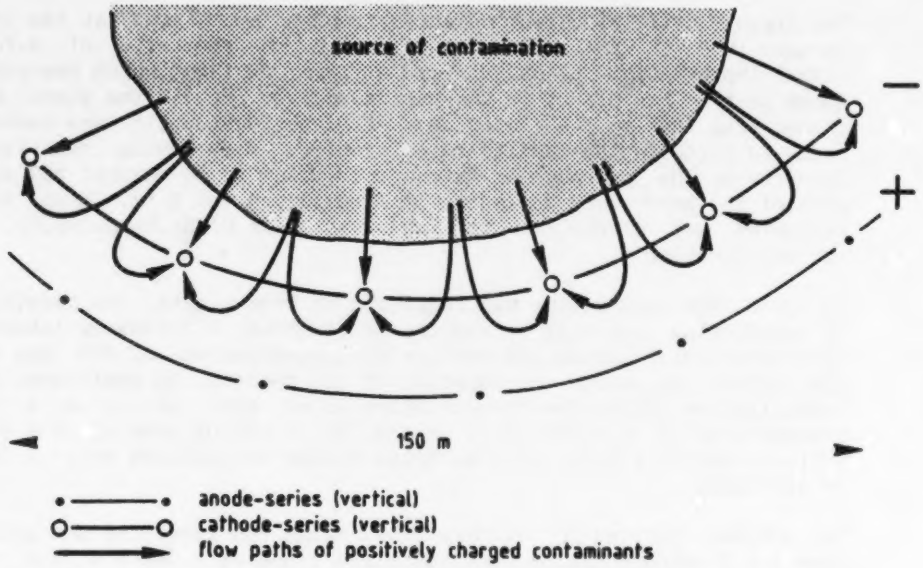

source of contamination
−
+
150 m
anode-series (vertical)
cathode-series (vertical)
flow paths of positively charged contaminants

Fig 7a. : Set-up of electrokinetical fence in soil with low permeability

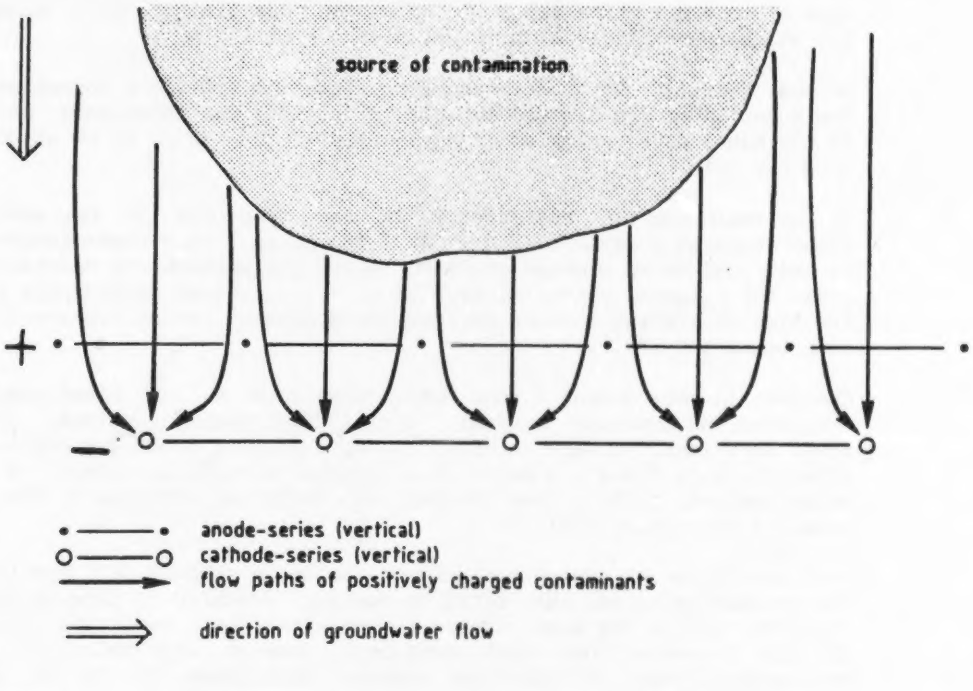

source of contamination
+
−
anode-series (vertical)
cathode-series (vertical)
flow paths of positively charged contaminants
direction of groundwater flow

Fig. 7b : Set-up of electrokinetical fence in soil with moderate to high permeability

Because of the time pressure it was decided tot continue the ER-process for another two weeks, whereafter the soil, which at that time would still show too high As-concentrations, would have to be excavated and removed. When the process was stopped on May 12 and the excavation began, many metal objects like tins, barrels, concrete-iron etc were found. These objects were supposed to hav been removed by the owner before the electro-reclamation started, but obviously, had failed to do so.

The discrepancy, therefore, between estimated and real energy-demand (and thus elapsed time) was caused by these metal objects, left behind in the soil. These objects function as preferential flow-paths for the electrical current and delay the movement of the pollutants in their vicinity, as first all the iron objects will go into solution.

Sample-point (1 m b.g.s.)	Metal	Concentration on 24/1/89	Concentration on 30/4/89	Energy (kWh/ton)
1	As	385	250	150
2		40	< 20	
3		250	< 20	
4		310	190	
5		50	< 20	
6		75	30	
7		40	< 20	
8		175	< 20	
9		40	< 20	
10		60	< 20	

Table 9.

Other applications

Electrokinetical fencing

The electrokinetical phenomena occurring when the soil is electrically charged, can also be used for fencing purposes. These so-called electrokinetic fences can be installed either at refuse-sites/factory complexes, where soil pollution has already been ascertained, or where soil pollution is likely to occur. Depending on the local geohydrological situation and the character of the soil, the elctrode configuration can be such that :

- the elctrokinetical transport is directed towards the source of the pollution (fig. 7a). The cathode-series is situated nearest to the source of pollution. Such a set-up should be applied in less permable soils without substantial groundwaterflow (< 1 m/year).

- the contaminants, which are carried along with the groundwater flow are diverted, collected around the electrodes and periodically removed. In this case the cathode-series is farthest away from the source of pollution and cathode- and anode-series are installed perpendicular to the direction of groundwater flow. Such a set-up should be applied when the soil and/or subsoil is relatively permeable (groundwaterflow velocity > 1 m/year).

Desalination of arable land

Salination of arable land is a common problem in those countries, where precipitation is generally low and evapotranspiration high. In combination with relatively high groundwater levels (coastal areas and river-lowlands), soils of low permeability and irrigation water with high total dissolved solids, the accumulation of salts in the top layers prohibits further agriculture.

The most common technique for landreclamation consists of the lowering of the groundwatertable and/or drainage of the soil by means of wells and/or horizontal drains. The soil is then frequently irrigated with relatively fresh water, thus leaching the salts from the soil. However the low permeability of the soil hampers more often than not the percolation of the leachate to the deeper layers.

By applying electrokinetical processes these problems can be overcome, as clay and argillaceous soils are specifically suited for electro-reclamation.

The As-remediation project mentioned afore showed, that after electro-kinetical treatment, the permeability of the heavy clay-soil had increased significantly. When furthermore gypsum is added at the anode-solution, the soil structure will be improved even more and higher crop production will be obtained (Collopy, 1958).

Cost estimates

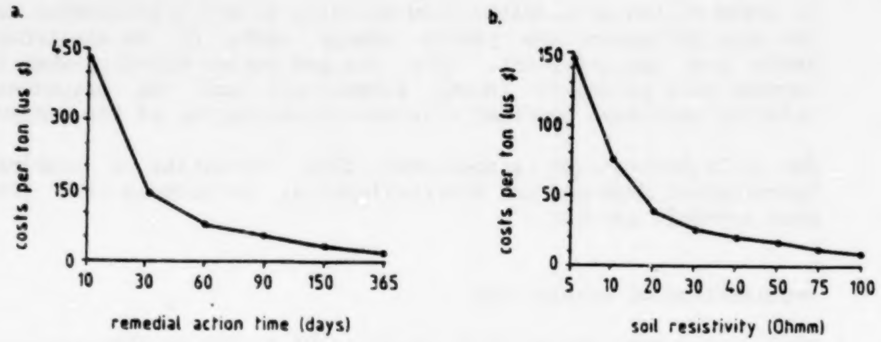
Electro-Recalamation

Fig. 8 shows a set of graphs depicting remediation cost per ton of soil as a function of remedial action time (fig. 8a) and as a function of the measure of contamination (fig. 8b), assuming a polluted area with dimensions of 500 m x 100 m x 1 m. From the graphs it is evident that short remediation periods and highly polluted soil (low resistivity) require a high amount of energy, having the greatest effect on the costs.

In practice, however, there is a limit to the electrical current which can be put into the soil. For every specific case, therefore, an optimum must be calaculated for energy supply and time duration.

Electrokinetical fencing

In fig. 9 the energy costs per year are given as a function of groundwater flow velocity (fig. 9a) and as a function of the rate of pollution (fig. 9b), assuming an electrokinetical fence of 500 m length and 10 m depth.

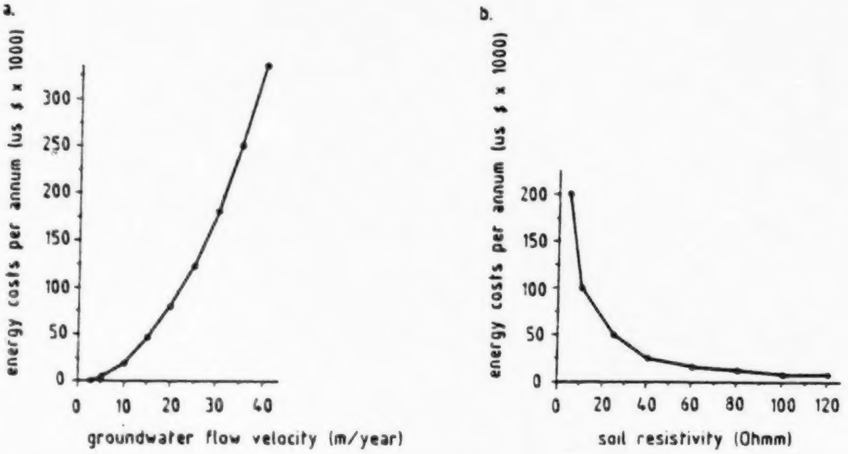


Assumptions:
- Area dimensions: 500 m x 100 m x 1 m
- Weigth of soil: 90,000 ton
- Distance between C- and A-series: 10 m
- Mutual distance anodes: 10 m

- Soil resistivity: 10 Ohmm

- Duration of ER-proces: 60 days

Fig. 8 : Cost estimate of electro-reclamation
a. costs per time-period
b. costs versus grade of pollution



Assumptions:
- Length of fence: 500 m
- Depth of fence: 10 m
- Average ion mobility: 1.56 $m^2/V \cdot year$

- Soil resistivity: 50 Ohmm

- Groundwater flow velocity: 10 m/year

Fig. 9 : Cost estimate of electrokinetical fencing
a. energy costs versus groundwater flow velocity
b. energy costs versus grade of pollution

In areas of low groundwater flow velocity (clay, argillaceous sand) and low soil pollution, the yearly energy costs of an electrokinetical fence are insignificant. This changes rather quickly, when the soil becomes more permeable (sandy formations) and the groundwater flow velocity increases together with the concentration of the contaminants.

For relatively high groundwater flow velocities a combination of hydrological measures and electrokinetical techniques will render the most economic results.

Desalination of arable land

Preliminary cost estimations amount to US $ 1000 to 2000 per ha.

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VACUUM EXTRACTION TECHNOLOGY

SITE Program Demonstration at Groveland Wells Superfund Site, Massachusetts

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Abstract

Vacuum extraction is an in-situ or ex-situ treatment process for cleanup of soils and groundwater contaminated with volatile organic compounds (VOCs), liquid-phase hydrocarbons or semi-volatile compounds. The process of removing VOCs from the vadose zone using vacuum is a patented process. Demonstration of the Vacuum Extraction Technology was conducted under the EPA Superfund Innovative Technology Evaluation (SITE) Program at the Groveland Wells Superfund site in Groveland, Massachusetts. The demonstration included an eight-week pilot test to removed VOCs (mostly TCE) from the underlying soil and groundwater.

The subsurface conditions included multilayered glacial deposits consisting of sands, silty sands and clays. Groundwater was 27 feet deep with a perched water table at about 10 feet. A multi-layered vacuum extraction and monitoring system was installed and operated sub-zero weather in northern Massachusetts.

Objectives of the pilot program included testing of soils before, during and after implementation of the vacuum extraction process. The effectiveness of the process was monitored by measuring subsurface vacuum, rates of flow, rates of VOC extraction and adsorption on activated carbon. The system was designed to operated on the fringe of the contaminant plume and to quantify the level of cleanup that could be achieved by the process by using barrier wells to prevent the migration of contaminants from the primary source area into the demonstration area.

Results demonstrated the effectiveness of the vacuum extraction process to clean up contaminated soils. Data from the pilot test also demonstrated that contaminant distributions were different than originally suspected from the Remedial Investigation (RI). In the area at the fringe of the contaminant plume, soil concentrations were reduced more than 95% to non-detectable levels. Accordingly, evaluation of the process dynamics and cleanup rates were adjusted to reflect the actual subsurface conditions. Additional data from subsequent cleanup work at the site is presented to further evaluate the demonstration program.

The objective of evaluating "How clean is clean?" is addressed with respect to the vacuum extraction process. Results from other sites where vacuum extraction has been applied is also presented. Results indicate that vacuum extraction technology is widely applicable for cleanup of soils and groundwater that are contaminated with VOCs.

INTRODUCTION

Vacuum extraction technology effectively removes volatile and semi-volatile compounds from soils and groundwater. Removal of liquid-phase hydrocarbons floating on the water table using vacuum extraction technology is faster and more effective than traditional approaches. Vacuum extraction is typically implemented in-situ, however, treatment of excavated soils on site using vacuum extraction technology is also effective. Groundwater can be removed simultaneously from vacuum extraction wells to further enhance recovery of groundwater contaminants and reduce the time frame for total cleanup.

Vacuum Extraction Technology was originally developed by Terra Vac. Since its inception more than five years ago, the technology has been widely used to cleanup soil and groundwater contaminated with volatile organic compounds (VOC). Two broadly applicable process patents exist that relate directly to vacuum extraction and the process of removing volatile contaminants from the vadose zone using vacuum (US Patent Nos. 4,563,760 and 4,665,039). Most successful applications of the technology require a license to use vacuum extraction to remove VOCs from the vadose zone.

Cleanup of contaminated soils using vacuum extraction is often the most important aspect of rapid, cost effective remediation at sites contaminated with volatile organics. A leaky tank or pipeline, surface spill, storage lagoon, landfill or other release can quickly contaminate a large volume of subsurface soil, rock and groundwater. Vacuum extraction removes contaminants directly from the source area, eliminating further migration in the subsoils. Implementation can be immediate, without risk of complicating future clean-up efforts.

The high incidence of soil contamination observed at underground storage systems, industrial and Superfund sites, and landfills requires that efficient and cost effective solutions be found to achieve cleanup objectives. Industrial experience with groundwater remediation has shown that where soils are contaminated and allowed to remain in place untreated, the groundwater cleanup process is costly and lengthy. Furthermore, without effective source control remediation, it is likely that the water resource may never again be used for a potable supply.

Demonstration of the Vacuum Extraction Technology was conducted under the EPA Superfund Innovative Technology Evaluation (SITE) Program at the Groveland Wells Superfund site in Groveland, Massachusetts. The demonstration included an eight-week pilot test to removed VOCs (mostly trichloroethylene) from the underlying soil and groundwater. Objectives and results of the pilot test are presented here. Results from other sites where vacuum extraction has been applied is also presented to further demonstrate the Terra Vac process is effective in cleaning up soil and groundwater to nondetectable levels.

VACUUM EXTRACTION PROCESS

Under normal static conditions within the soil matrix, VOCs are partitioned between four possible phases: 1) vapor, 2) liquid, 3) dissolved in soil water, 4) adsorbed to solid particles. These four phases define the aggregate contaminant concentration in the subsoils.

The vapor phase partitioning is a complex function of water content, organic content, solubility, temperature and vapor pressure. It is not necessary to define the exact relationship between soil concentration and vapor concentration as a function of time in order to understand that reductions in extracted vapor concentrations are driven by continuous partitioning to the vapor phase which corresponds to reductions in soil concentrations. Furthermore, as concentrations in soils are reduced significantly, vapor phase partitioning is generally controlled by Henry's Law.

As vast volumes of soil vapor are removed by the vacuum process, fresh air naturally recharges the vadose zone from the surface. Fresh air moves through the contaminated zone as VOCs are partitioned from the soil matrix to the vapor phase and move to the extraction wells. With vacuum induced volatilization and air stripping of the soil matrix, cleanup occurs continuously.

As contaminant vapors are removed from the subsoils pore volume, the three other phases (liquid, adsorbed and dissolved) of VOCs vaporize in place, further reducing the aggregate soil concentration. Since VOCs vaporize readily, the vacuum extraction process continually drives the contaminants within the soil matrix to the vapor state.

Progress of the vacuum extraction soil decontamination system can be monitored by the concentration of the extracted vapors. Since vaporization occurs rapidly within the soils, the soil vapors beyond the immediate vicinity of the extraction well are near equilibrium with respect to the majority of the contaminants contained in the soil matrix.

As VOCs are vacuum extracted from the subsoils, the removal rate declines with time, indicating cleanup of the soils. During the vacuum extraction process, vapors extracted at the wellhead represent essentially an aggregate soil-gas concentration near the screened interval. Under static conditions, the concentration of VOCs in the vapor phase is proportional to the aggregate contaminant concentration in the soil.

The first step of vacuum extraction design is delineation of the extent and magnitude of the soil contamination and liquid-phase contaminants that may be floating on the water table. Vacuum extraction wells are designed with a vacuum-tight seal near the surface and an extraction zone (screen) corresponding to the profile of subsurface contamination.

The spacing of vacuum extraction wells is critical to efficient remediation. Depending on the depth to groundwater and soil type, the radius of influence of an extraction well can range from tens of feet to hundreds of feet. Soil permeability, porosity, moisture content, stratigraphy and depth to groundwater are important factors in determination of the radius of influence.

Vacuum extraction technology is effective in treating soils containing virtually any chemical with a volatile character. All of the volatile priority pollutants and many of the semivolatiles have been successfully extracted with the vacuum process. However, metals (except mercury), heavy oils and PCB's will remain in place as the volatile compounds are extracted by the process. . Dual vacuum extraction of groundwater and vapors has been effective at restoring groundwater quality to drinking water standards within short periods of time.

For those sites with numerous types of compounds (i.e., VOCs, PCB, pesticides and metals) a phased approach is often required. In these cases, it is prudent to remove VOCs first using vacuum extraction so that other technologies can then be applied more cost effectively and safely. For example, chemical treatment or incineration of soil, which require excavation, the health risk of excavation is minimized if the majority of VOCs are removed first, in-situ, by vacuum extraction. Many methods used to chemically stabilize metals are more effective after vacuum extraction has removed VOCs.

Vacuum extraction is an effective means of removing hydrocarbons floating on the water table. Compared to typical double-pump systems, skimmer pumps and air displacement total-fluids product recovery systems, vacuum extraction is faster, more effective and low cost per gallon of product removed. Liquid-phase hydrocarbons are removed without pumping groundwater so that separation and treatment of large volumes of contaminated water is eliminated.

Where contaminants are within the saturated zone and groundwater is relatively shallow (i.e., less than 30 feet deep) a "dual extraction" approach is effective. Dual extraction is a term used to describe the process of simultaneously extracting groundwater and vapors under vacuum using the same well. In the simplest form, operating a submersible pump within a vacuum extraction well will lower the water table and increase the effective unsaturated zone in which the vacuum extraction process will vaporize contaminants.

Simultaneous extraction of groundwater and vapors under vacuum has several benefits that enhance the rate of groundwater cleanup. First, the rate of contaminant removal increases compared to groundwater extraction alone since contaminants have two pathways for removal: aqueous phase and vapor. Even in areas where groundwater movement beneath the water table is the only source of contamination, the dual extraction process often yields the same mass flux (i.e., pounds/day) from the vapor phase as the aqueous phase. This indicates that substantial partitioning is occurring in the transition zone and capillary fringe. In medium to low permeability aquifers the maximum rate at which groundwater can be extracted from a given well increases two to three fold using dual extraction. The net effect of these two phenomena can yield a six-fold increase in the overall contaminant removal rate, and hence, a six-fold reduction in the time required to reach clean-up objectives.

Subsurface Conditions at the Demonstration Site

The Groveland site is underlain by glacial deposits. The thickness of the unconsolidated deposits under the site is on the order of 32 to 50 feet. In the pilot test area the upper 10 to 16 feet consist of fill and glacial outwash sands. A dense clay layer, 3 to 7 feet thick, is observed below the sands, but is discontinuous throughout the site. Glacial till is present below the clay. The water table is roughly 25 feet deep in the test area.

A multi-layered vacuum extraction and monitoring system was installed, as shown in Figure 1, to segregate the upper sand zone from the lower till. The vacuum extraction system consisted of four extraction wells and four monitoring wells; each was capable of extracting contaminants separately from above or below the clay. This provided effective hydraulic separation of the two more permeable units (sand and till) and allowed differentiation of the contaminants extracted from the two zones. Activated carbon was used to control emissions from the site.

Volatile organic soil contamination is generally constrained within soils above the clay lens, according to the Record of Decision. The contamination begins just below land surface and extends down to the top of the clay lens. Below the clay lens contamination levels are generally less than 100 ppm. However, one "hot spot" of soils containing 1500 ppm was observed distant from the major source area and below the clay. The primary source area was considered to be beneath the storage area of the manufacturing building located at the site. Accordingly, the SITE demonstration was designed to focus on the periphery of the primary zone of contamination.

Pilot Test Objectives

The objectives of the pilot test was to demonstrate the vacuum extraction technology would effectively:

- remove VOCs from the vadose zone,

- remove VOCs from various soil type (sands and clays),
- correlate declining recovery rates and cleanup levels,
- correlate VOC concentrations in soils with extracted vapors.

Several constraints were imposed that impacted the design and operation of the vacuum extraction system. One constraint was to not clean up the site, although it was important to demonstrate how clean the process could decontaminate the soils. In addition, the time frame for cleanup had to be relatively short in order to minimize costs.

The size of the soil volume to be treated was difficult to contend with since the in-situ treatment process did not lend itself to segregating the subsurface treatment process to a small test area. Evaluating the effects of the subsurface dynamics and the objective of judging "How clean is clean?" was a challenge for the short term, in-situ demonstration.

The location of the vacuum extraction pilot test was selected to minimize interference with the on-site manufacturing operations, to be near the edge of the contamination, and to be accessible during the mid-treatment and post-treatment sampling. Since the contamination was wide-spread but predominantly located beneath a building at the demonstration site, it seemed plausible to install a line of vacuum extraction wells to act as a "barrier", isolating the high level contamination from an extraction well installed in the less contaminated area, thus, focusing the evaluation on the effectiveness achieved in the low level concentration area. The presumption was that the contaminant distribution was sufficiently defined to predict the movement of contaminants in the subsurface during the demonstration.

The final objective in the SITE demonstration for the vacuum extraction technology was to evaluate "How clean is clean?" Several test methods were used including TCLP, soil concentrations (headspace and Contract Laboratory methods), shallow soil gas surveys and monitoring subsurface contaminant vapor concentrations with time.

RESULTS

The subsurface contaminant plume within the soils in the demonstration area was erratic and somewhat different from the data available from the Remedial Investigation. The highest concentration measured during the baseline sampling of the demonstration was within the presumed "clean" zone. The extraction well from the presumed "cleaner" area recovered more VOCs than a barrier well located closer to the primary source area. This critical difference between actual and presumed conditions required a refocusing of the results with respect to the barrier design and actual results achieved.

Recovery rates from vacuum extraction wells varied significantly, ranging initially from 9 to 77 pounds/day. Higher recovery rates were obtained from the shallower zone where the highest soil concentrations were observed. Recovery rates decline with time except where the contaminants were extracted from the wells near the primary source area.

During the SITE demonstration, Terra Vac removed about 1300 pounds of VOCs from the subsoils during the eight week pilot test. These data were derived from flow and concentration measurements taken during the vacuum extraction test. The results were confirmed by analysis of the activated carbon that was used to collect extracted VOCs.

Results of the demonstration indicated contaminant levels in soils on the order of 10 ppm were reduced to non-detectable levels, as depicted in Figure 2. In areas with higher contamination (i.e. greater than 100 ppm in soil) contaminant concentrations in soils were reduced about 96% during the 8 week pilot test.

In general, reductions in VOC concentrations throughout the shallow soils at the site were observed. Figure 3 shows that a substantial reduction (to non-detectable in many areas) in soil concentration was achieved in both the clays and the silty sands within the short treatment period. The average reduction in VOC concentrations in clay soils where significant contamination was present was reduced about 97%. Similarly, in sands concentrations were reduced 89%.

Shallow soil gas surveys before, at mid-point and after treatment indicated consistent reductions in concentrations. Figures 4 and 5 shows the dramatic reduction in concentrations observed by this method.

Steady declines in extracted vapor concentrations were observed in both the extraction wells and the monitoring wells during the pilot test. The wells which weren't affected by the primary source area showed the greatest reduction in vapor concentrations both in the shallow extraction zone and the deep extraction zone. In general, higher extraction rates were observed in the shallow soils compared to the deep zone.

Correlation between the soil concentration and the extracted vapor concentration was difficult due to the heterogeneities in soil concentrations at the beginning of the treatment process. At other sites where complete vacuum extraction systems are implemented, better correlations have been achieved.

Overall, the Terra Vac Vacuum Extraction Process was successfully demonstrated in the EPA SITE Program. Cumulative extraction of VOC was 1300 pounds as depicted in Figure 6. As a result of this successful demonstration Terra Vac is currently continuing the cleanup for the owner of the manufacturing facility on the site.

Cleanup Objectives

Terra Vac has applied Vacuum Extraction Technology at numerous sites to achieve various cleanup levels. Since cleanup objectives in soils are generally site specific, several examples of cleanup objectives and results of the vacuum extraction process achieving these objectives are presented below.

Based on the data from the SITE demonstration it is estimated that full scale cleanup can be achieved to 50 ug/kg using vacuum extraction within about one year of operation. The cleanup objectives for TCE in the soils have been designated by EPA in the ROD at 6.3 ug/kg. Extrapolating the level of cleanup from the data from the SITE demonstration, complete cleanup would probably occur within about two years.

Florida Department of Environmental Regulation (FDER) has defined a excess soil contamination as 500 ppm of hydrocarbons in headspace of a sealed container of soil. The concentration extracted from the wellhead may be considered essentially an aggregate "headspace" concentration of hydrocarbons in the soils around the well screen so that the 500 ppm hydrocarbon response would represent the upper limit of a cleanup goal. Lower values may be required at certain sites in order to protect groundwater resources. Application of the Terra Vac Process at a site in Florida demonstrated the capability of the process to meet the FDER cleanup objective in about 6 months of operation, removing over 20,000 pounds of hydrocarbons during the process.

An alternative criteria for considering the cleanup goal would be based on a drinking water standard for indicator parameters and correlate to an extracted vapor concentration. For example, the lowest Maximum Contaminant Level in Florida is 1 ug/l for benzene. Goals for cleanup of the vadose zone may be considered using the concentration of benzene in the soil water or pellicular water just above the water table and Henry's Law to calculate the vapor concentration.

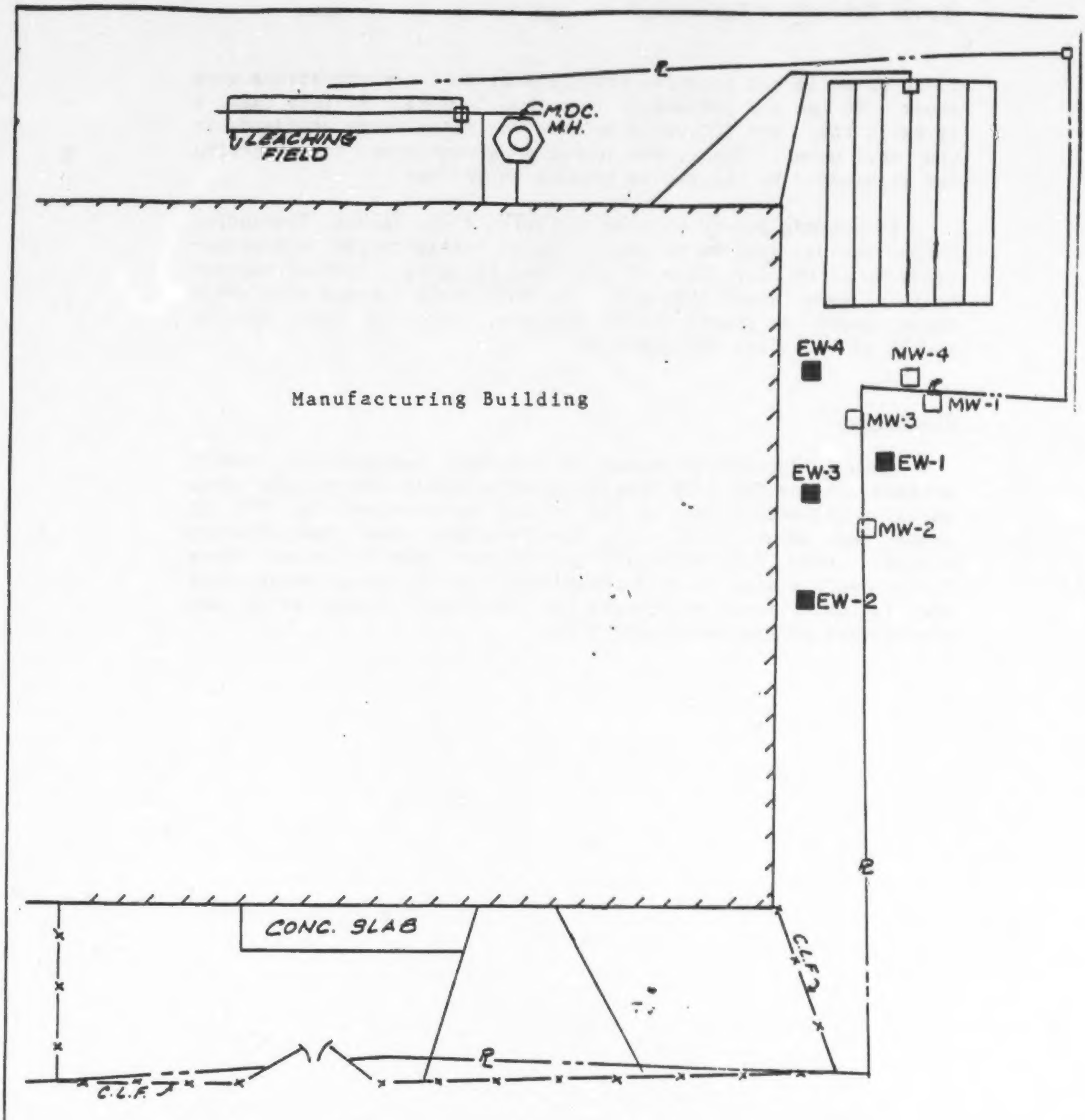
Based on a measured Henry's Law Constant for benzene, the soil gas concentration in equilibrium with water at 1 ug/l would be about 0.18 ug/l or 0.05 ppm benzene in air. Assuming the extracted vapors from the wellheads are sufficiently close to equilibrium conditions, an area within the radius of influence of the well may be considered clean if the concentration of extracted benzene vapors is less than 0.05 ppm. This objective was also met during the FDER demonstration after about six months of vacuum extraction by Terra Vac.

At an industrial site in South Carolina the same concept was applied to lower TCE concentrations in soil to below levels that would impact groundwater quality. Terra Vac utilized Vacuum Extraction Technology with the dual vacuum extraction approach to clean up soils and groundwater. Initial soil concentrations were about 300 ppm and reduced to less than 1 ug/kg. At less than 1 ug/kg in soil, the TCE would be below drinking water standards in the soil water. Hence, the source of groundwater contamination was eliminated by the vacuum extraction process.

At another Superfund site in Puerto Rico, Vacuum Extraction Technology was applied to reduce carbon tetrachloride concentrations in silty clay soils to less than 10 ug/kg. Initial concentrations were above 2000 ppm. The full scale cleanup took about three years of operations to complete, removing over 100,000 pounds of VOCs from the subsoils.

Conclusion

Vacuum Extraction Technology has been successfully demonstrated in the EPA SITE Program to effectively remove VOCs from soils. Concentrations of TCE in soil were reduced by 89% in sands and about 96% in clays for the eight week demonstration period. Data from this site and the more than 70 sites where Terra Vac has applied this technology clearly demonstrates that the Vacuum Extraction Process can completely treat soils and groundwater contaminated with VOCs.


LEACHING FIELD
C.M.D.C. M.H.
Manufacturing Building
EW-4
MW-4
MW-1
MW-3
EW-1
EW-3
MW-2
EW-2
CONC. SLAB
C.L.F.
C.L.F.

LEGEND

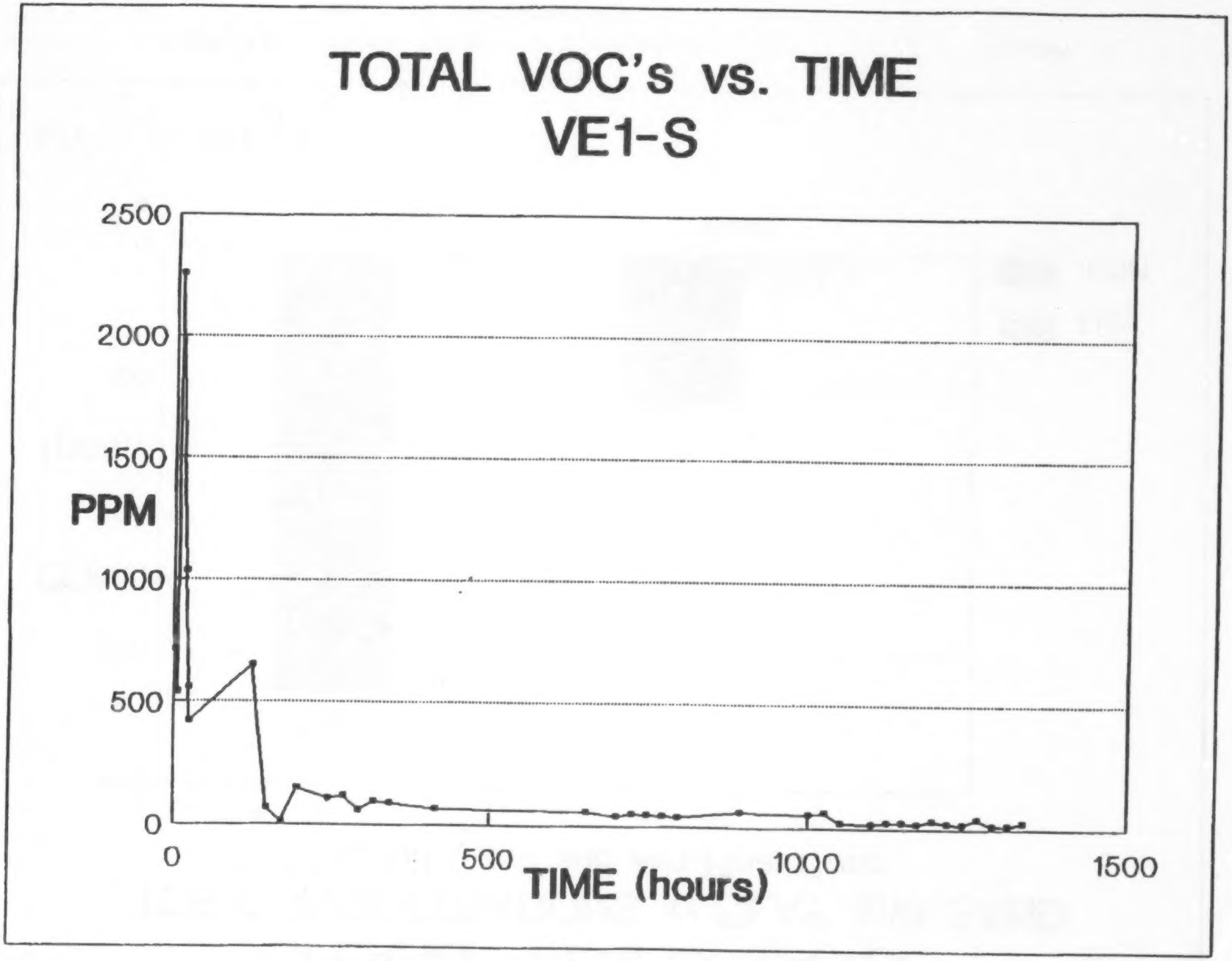
EW-1 ■ SOIL VAPOR EXTRACTION WELL

MW-5 ☐ SOIL VAPOR MONITORING WELL

TERRA VAC
EPA SITE DEMONSTRATION

SITE PLAN
FIGURE NO. 1

VACUUM EXTRACTION TECHNOLOGY



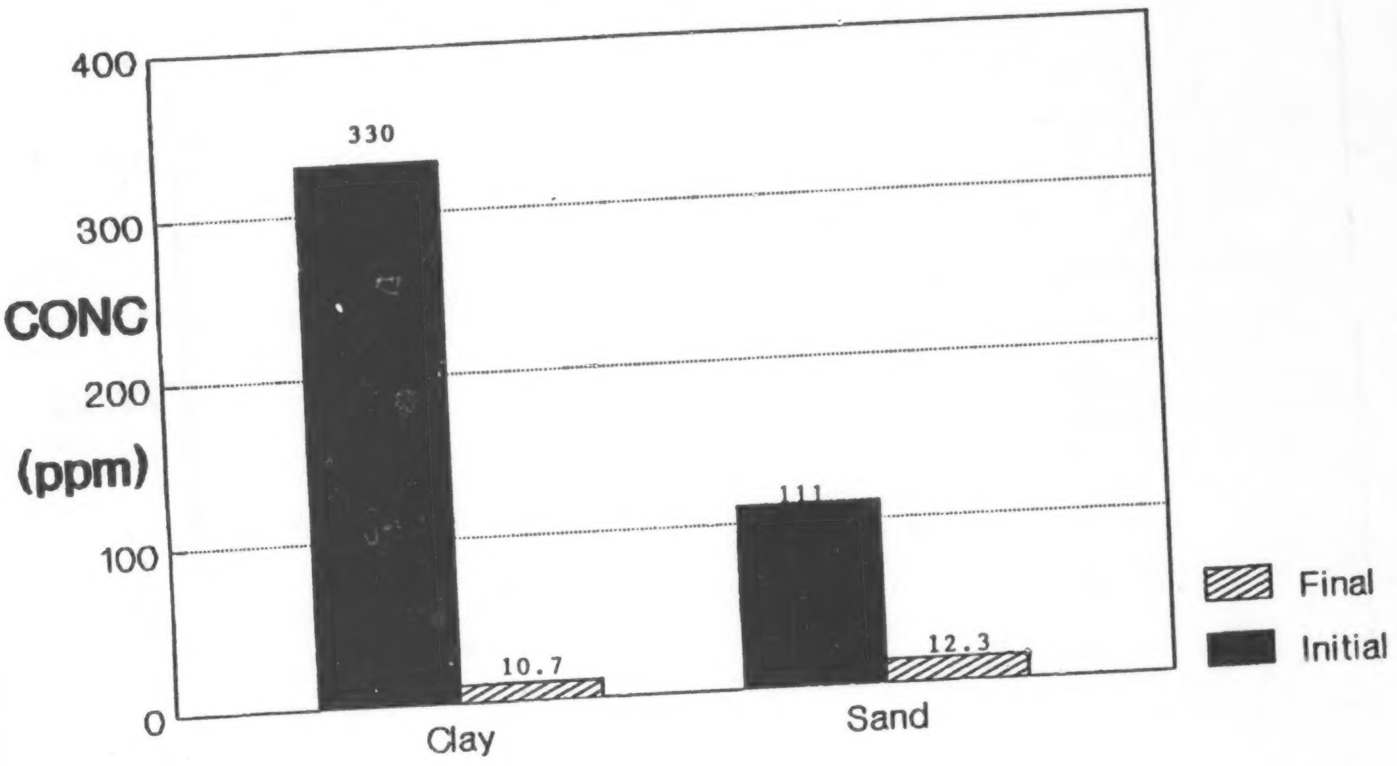
TERRA VAC VACUUM EXTRACTION TECHNOLOGY
EPA SITE DEMONSTRATION

FIGURE 2

CLEANUP PERFORMANCE

TCE CONCENTRATIONS in CLAY and SAND

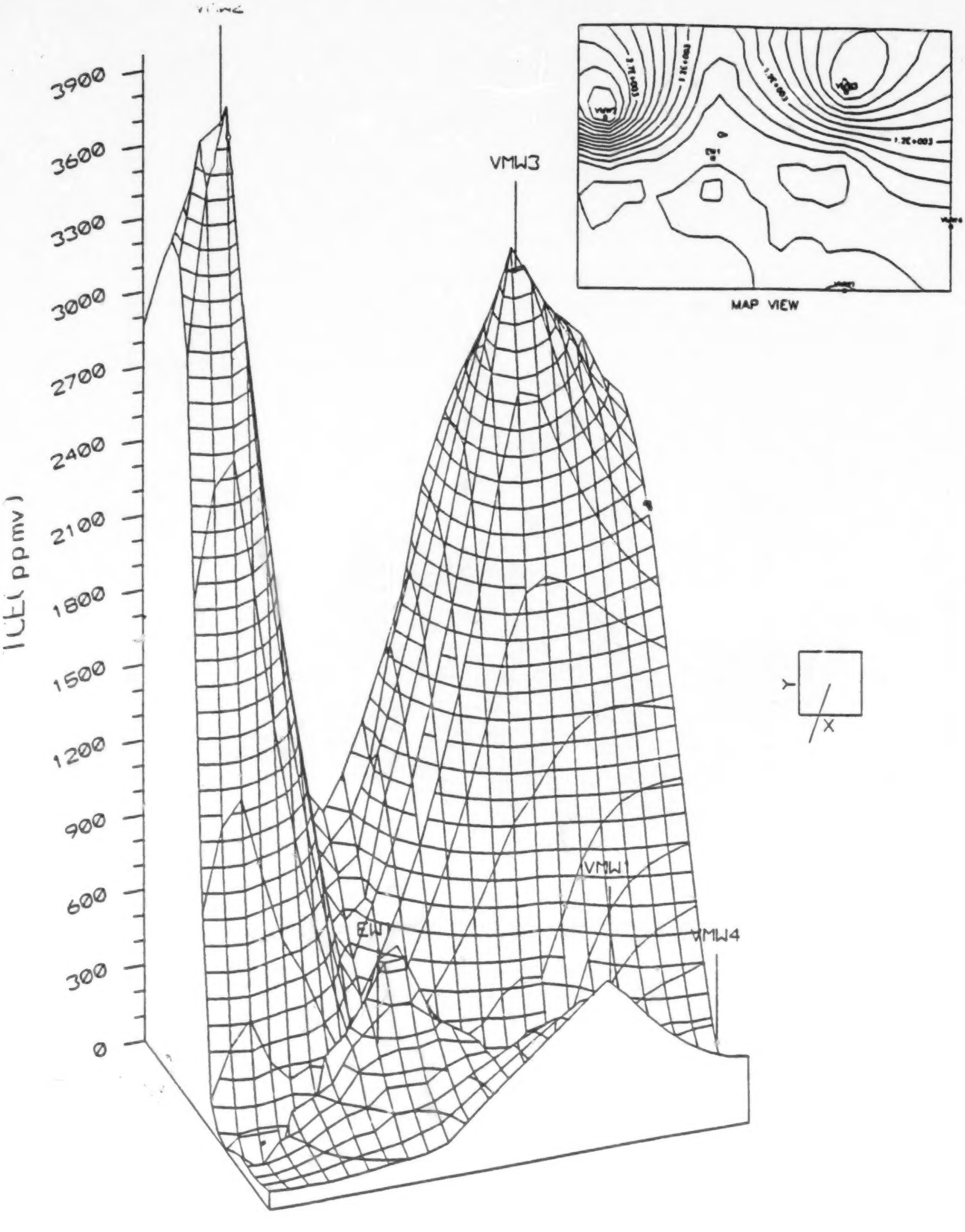
Avg Init Conc and Avg Final Conc



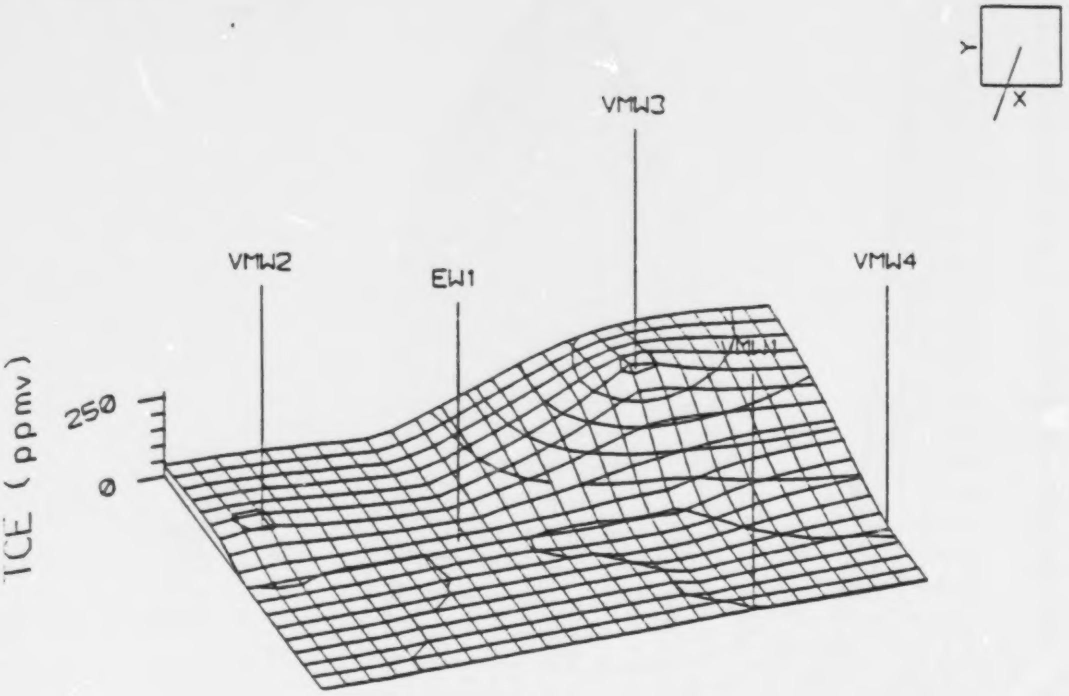
MW - 3 and EW - 4

FIGURE 3

TERRA VAC VACUUM EXTRACTION TECHNOLOGY
EPA SITE DEMONSTRATION



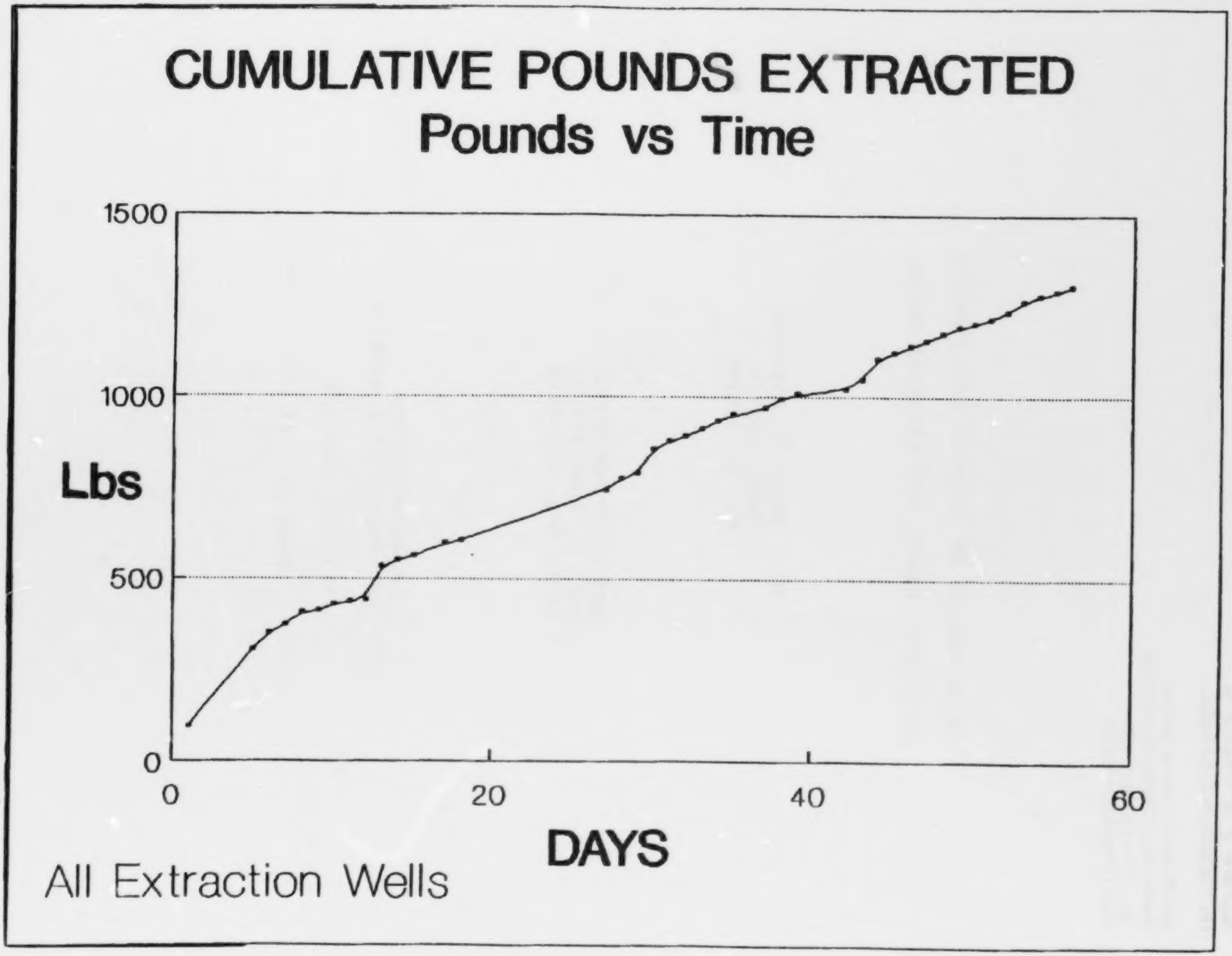
PRETREATMENT SHALLOW SOIL GAS CONCENTRATION



POSTTREATMENT SHALLOW SOIL GAS CONCENTRATION

TERRA VAC VACUUM EXTRACTION TECHNOLOGY

EPA SITE DEMONSTRATION FIGURE 5



TERRA VAC VACUUM EXTRACTION TECHNOLOGY FIGURE 6
EPA SITE DEMONSTRATION

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UV/OXIDATION OF ORGANIC CONTAMINANTS IN GROUND, WASTE, AND LEACHATE WATERS

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INTRODUCTION

The removal of low levels of organic contaminants from groundwaters and industrial wastewaters presents a challenge to environmental professionals. Well-known and commonly used treatment processes such as granular activated carbon (GAC) and air-stripping transfer pollutants from one medium to another. With increasing public and regulatory concern over the final fate of pollutants, such transference technologies are not optimal.

Conventional chemical oxidation has been used in the treatment of various waters polluted by organic chemicals for a number of years. Potassium permanganate, chlorine and chlorine dioxide have been used for treating organics such as phenol and its homologs in wastewaters. Hydrogen peroxide with a catalyst such as ferrous sulfate (Fenton's Reagent) has been used for oxidizing phenol and other benzene derivatives. Processes utilizing iron catalyzed peroxides and chlorine compounds are attractive in that they utilize relatively low-cost treatment equipment. The disadvantages of these processes are that they can attack only a limited number of refractory organics, and they produce iron sludges or chlorinated organics. Ozone alone has been used to treat phenolic wastes, cyanides and certain pesticides. Ozone treatment is a very clean process but is limited in the number of compounds which can be treated. These oxidation processes have been used and are continuing to be used in a number of situations.

The use of ultraviolet light catalyzed ozone plus hydrogen peroxide (UV/oxidation) as a water treatment technique is rapidly expanding. It offers a means of solving many of the problems created by the toxic water soluble organic chemicals that are found today in groundwater, wastewater, leachate and drinking water supplies without many of the disadvantages of more conventional treatment techniques.

UV/oxidation, when used as a stand-alone treatment process, or in tandem with some of the above mentioned processes, can cost-effectively destroy or render non-toxic the organic chemicals found on the EPA's priority pollutant list.

This paper describes the experience of Ultrox International in developing and applying the ULTROX® UV/oxidation process to the full-scale treatment of organic chemicals in wastewaters, drinking waters, leachates and groundwaters. The oxidants used in these applications are ozone and hydrogen peroxide. Ultrox International was issued a process patent in 1988 covering the application of UV light, ozone and hydrogen peroxide to the treatment of a broad range of organic compounds in water.

DESCRIPTION OF THE UV/OXIDATION PROCESS

The ULTROX® process was developed over a 15 year period. Ultraviolet light, when combined with O_3 and/or H_2O_2 produces a highly oxidative environment significantly more destructive than that created with O_3 or H_2O_2 by themselves or in combination.

UV light significantly enhances ozone or H_2O_2 reactivity by:

I. Transformation of O_3 or H_2O_2 to highly reactive $(OH)^-$ radicals

II. Excitation of the target organic solute to a higher energy level

III. Initial attack of the target organic by UV light

The importance of the conversion of the ozone or H_2O_2 to $(OH)^-$ can be more easily understood after studying the relative oxidation power of oxidizing species. Hydroxyl radicals have significantly higher oxidation power than either hydrogen peroxide or ozone.

Species	Oxidation Potential Volts	Relative Oxidation Power*
Fluorine	3.06	2.25
Hydroxyl Radical $(OH)^-$	2.80	2.05
Atomic Oxygen	2.42	1.78
Ozone	2.07	1.52
Chlorine Dioxide	1.96	1.44
Hydrogen Peroxide	1.77	1.30
Perhydroxyl Radicals	1.70	1.25
Hypochlorous Acid	1.49	1.10
Chlorine	1.36	1.00

* based on chlorine as reference (= 1.00)

The effect of UV enhanced oxidation is illustrated in Table 1.

ULTROX® UV/OXIDATION EQUIPMENT

ULTROX® UV/oxidation equipment treatment systems: (1) have very few moving parts, (2) operate at low pressure, (3) require a minimum of maintenance, (4) operate full-time or intermittently in either a continuous or batch treatment mode, (5) utilize efficient, low temperature, long life UV lamps, and (6) can employ the use of a micro-processor to control and automate the treatment process.

The ULTROX® UV/oxidation system consists of a UV/oxidation reactor and an oxidation source -- either an ozone generator with an air preparation system and/or a hydrogen peroxide feed system. Figures

1 and 2 show an isometric assembly view and drawing of a Model F-650 system, which accommodates flow rates up to 60 gpm or batches of 650 gallons.

The reactor is fabricated from stainless steel. The UV lamps are enclosed within quartz tubes for easy replacement and are mounted vertically within the reactor. Depending upon size of the reactor and the type of water to be treated, the reactor can have 4 to 8 stages. Lamps are installed either in all stages or in designated stages, depending upon the type of treatment specified. When ozone is used as the oxidant, it is introduced at the base of the stage. The ozone is dispersed through porous stainless steel diffusers. The number of diffusers needed will depend upon the type of organics being oxidized and the degree of removal required.

Ozone is produced from either compressed air, dried to a -60°F dewpoint by desiccant columns, or produced from cryogenic oxygen. Up to 2% wt. ozone is generated from air, and up to 5% wt. ozone can be produced economically from oxygen.

When hydrogen peroxide is used in the process, it is directly metered into the influent line to the reactor.

Within the reactor, the water flows from stage to stage in a sinusoidal path using gravity flow. When the reactor uses ozone, the residual ozone in the off-gas is decomposed back to oxygen by the use of a fixed-bed catalytic unit operating at 150°F. The air is then vented to the atmosphere.

Ozone generators with varying capacities are used with the Model F-650 reactor. The size of generator depends upon the ozone dosage requirements. Present installations use 28 to 140 lb. per day capacities.

APPLICATION OF UV/OXIDATION

UV/oxidation equipment developed by Ultrox in recent years has been used to treat a wide variety of waste streams. Tables 2 and 3 list toxic compounds found in groundwaters and wastewaters that have been successfully treated with the ULTROX® UV/oxidation System. Specific case histories of treatability and design studies for private industries and military installations are presented in Table 4. In each of these cases, pilot treatment plants were operated on site to develop treatment design and economic data.

Contaminates oxidized included: pesticides, petroleum compounds, munitions, and chlorinated solvents.

Table 5 illustrates projects where the treatability and design studies were converted into permanent on-site UV-oxidation installations. The systems to date treat either industrial groundwaters, wastewaters and process waters. Contaminants in these waters include phenols, chlorinated solvents, hydrazine, dimethylnitrosamine, tetrahydrofuran and formaldehyde. Commercial systems have been designed, built and installed to treat flows varying from 10,000 gallons to 300,000 gallons per day. A system to treat 1.3 million gallons per day is under construction.

Standard equipment designs are used in all of these installations. Reactor size varies from 300 gallons to 4,300 gallons. Ozone generators range from 21 lb. to 140 lb per day. In several cases hydrogen peroxide is used in place of or with ozone.

Treatability studies are carried out first in the laboratory using glassware equipment to determine the feasibility of treating the water with UV/O_3, UV/H_2O_2, or $UV/O_3/H_2O_2$.

If the results are encouraging, the next step in the study involves the installation of a skid-mounted pilot plant on site. Sufficient design and economic data normally are collected within 2 weeks. Specifications for the full-scale system are then prepared. Standard reactors, ozone generators and hydrogen peroxide feed systems are utilized. Systems are assembled and tested at our facilities and then shipped to the job site. The systems are then installed, checked out, and turned over to the customer. Full service maintenance contracts are available.

Full-scale systems, in most cases, are automated using microprocessor control. The system usually requires periodic monitoring (once per shift or once per day). The systems are designed to operate in a batch or continuous mode depending upon treatment requirements.

In a number of cases, UV-oxidation is used as a part of a treatment train. For example, at wood treating sites prior to the UV-oxidation treatment, the wastewater or groundwater requires breaking of oil/water emulsions and removal of suspended matter, as well as adjustment of pH.

CASE STUDY: EPA SITE PROGRAM - LORENTZ BARREL AND DRUM SITE, SAN JOSE, CA

The EPA has established a formal program to accelerate the development, demonstration, and use of new or innovative technologies to be used in site cleanups. This program, called the Superfund Innovative Technology Evaluation (SITE) program, has four goals:

- To identify and, where possible, remove impediments to the development and commercial use of alternative technologies.
- To conduct a demonstration program of the more promising innovative technologies for the purpose of establishing

reliable performance and cost information for site characterization and cleanup decision-making.

- To develop procedures and policies that encourage selection of available alternative treatment remedies at Superfund sites.
- To structure a development program that nurtures emerging technologies.

Each year, EPA solicits proposals to demonstrate innovative technologies. To identify the best available technologies, an extensive solicitation is necessary. A screening and selection process follows, based on four factors: (1) the technology's capability to treat Superfund wastes, (2) the technology's performance and cost expectations, (3) the technology's readiness and applicability to full-scale demonstrations, and (4) the developer's capability and approach to testing.

In the third year of the SITE program, Ultrox was selected to demonstrate their UV/oxidation technology. The Lorentz Barrel and Drum Superfund site in San Jose, California was selected for the demonstration.

The Lorentz site was used for drum recycling for nearly 40 years. Over this period of time, the site received drums from over 800 private companies, military bases, research laboratories, and county agencies in California and Nevada. Drums arrived at the site containing residual aqueous wastes, organic solvents, acids, metal oxides, and oils.

Since 1968, there have been several regulatory actions at the Lorentz site. In 1987, the Lorentz facility ceased operation and the EPA assumed lead agency responsibility for the site remediation. Investigations revealed that the groundwater beneath the site was contaminated with a number of chlorinated solvents, chlordane, toxaphene and PCBs.

An ULTROX® P-150 pilot plant was moved in on February 21, 1989. Thirteen (13) tests were conducted between February 24 and March 9, 1989, on extracted groundwater from the site. During the treatability bench studies, TCE, TCA, and DCA were chosen to monitor the progress of the pilot.

Figures 3, 4 and 5 illustrate analyses of the waste stream influent and the treated effluent for the targeted contaminants.

The final report has not yet been issued by the EPA. However, based on the preliminary results, the ULTROX® UV/oxidation process was successful in the reduction of all of the VOCs present in the groundwater at the Lorentz site to below drinking water standards.

The bicarbonate level of the groundwater was extremely high (1200 mg/l). Because of this, treatment costs are higher than what would be experienced in more normal groundwater applications. Based on the conditions tested at the site, treatment costs were estimated to be as follows:

Flow Rate: 100 gpm
Influent Concentration: 250-1000 μg/l VOCs, pesticides, PCBs
Effluent Concentration: <10 μg/l

Treatment Costs:	$/1000 gallons
Ozone (@ 0.06/KWH)	$ 0.370
H_2O_2 (@ $0.75/lb)	0.156
UV (incl. power and annual lamp replacement	0.836
O & M Cost	1.36
Capital Amortization (16%/year)	0.75
Total Treatment Cost:	$ 2.11/1000 gallons

CASE STUDY: AUTOMOTIVE PARTS MANUFACTURER, MICHIGAN

Testing of water beneath a Michigan automotive parts manufacturer revealed significant VOC contamination. TCE levels of 5,000 to 10,000 μg/l were recorded as well as trace levels of other chlorinated solvents. The Michigan Department of Natural Resources required that the manufacturer pump and treat the groundwater.

The manufacturer investigated air stripping with GAC off-gas treatment, aqueous phase GAC and ULTROX® UV/oxidation as possible treatment alternatives. Bench scale studies were conducted at a GAC supplier and at Ultrox's laboratory. While all treatment techniques could provide the required removal levels, UV/oxidation was the most economical. An ULTROX® P-75 pilot scale treatment system was delivered to the site. Testing over a two week period confirmed the data obtained in the laboratory. An ULTROX® F-3900 treatment system was ordered and installed in May, 1989. The system is currently operating and achieving the following results, which exceed Michigan requirements:

Flow Rate: 210 gpm
Influent Concentration: 5500 μg/l TCE
Effluent Concentration: 1 μg/l TCE

Treatment Costs:	$/1000 gallons
Ozone (@ 0.06/KWH)	$ 0.119
H_2O_2 (@ \$0.75/lb)	0.188
UV (incl. power and annual lamp replacement	0.133
O & M Cost	0.44
Capital Amortization (16%/year)	0.29
Total Treatment Cost:	$ 0.73/1000 gallons

UV/OXIDATION TREATMENT AND OPERATING COSTS

Table 6 represents the direct operating and maintenance costs for treatment of contaminants in groundwater at water utility sites. The costs are based upon pilot plant studies at four different sites in Southern California. At three of the sites, perchloroethylene (PCE) and trichloroethylene (TCE) were the contaminants with concentrations ranging from 20 ppb to 200 ppb.

Table 7 presents the actual costs of treating by UV/oxidation wastewater and groundwaters at various permanent industrial installations. Some of these costs are in the cents per thousand gallon range and others in cents per gallon range.

In the case of the hydrazines, a small volume of water is treated per day on a batch basis and a comparatively long reaction time is needed. UV/oxidation was found to be the most cost-effective method of destroying the three types of hydrazines and the nitrosamine which is formed as a by-product by the oxidation. The UV/oxidation system replaced a chlorination unit, which produced chlorinated organic by-products.

The price range of UV/oxidation equipment at various installations cited in Table 8 varies from $45,000 to $300,000 (uninstalled). Pricing depends upon the oxidant requirement - whether ozone or hydrogen peroxide is used, the chemical structure of the organic compounds treated, the number of UV lamps required, and the retention time required to achieve an acceptable discharge standard.

SUMMARY

Over the last 15 years, UV/oxidation has progressed from research and development to commercial operation. During these years, Ultrox has advanced its design through applied bench testing, pilot studies, and full-scale systems that remove contaminants from a wide variety of wastewaters and groundwaters.

UV/oxidation technology is not suitable for every organic contamination problem. It can, however, effectively address a wide range of clean-up needs. This form of on-site chemical oxidation can offer real advantages over conventional treatment techniques and should be considered when evaluating water treatment alternatives.

TABLE 1

OXIDATION OF METHYLENE CHLORIDE

TIME (MIN.)	CONTROL	UV	UV/H_2O_2	O_3/H_2O_2	UV/O_3	UV/O_3/H_2O_2
0	100	100	100	100	100	100
15	100	59	46	32	36	19
25	100	42	17	21	16	7.6

OXIDATION OF METHANOL

TIME (MIN.)	CONTROL	UV	UV/H_2O_2	UV/O_3	UV/O_3/H_2O_2
0	75	75	75	75	75
30	75	75	75	31	1.2

CONCENTRATIONS = mg/l

TABLE 2

Industrial effluents containing:

- Amines
- Analine
- Benzene
- Chlorinated Solvents
- Chlorobenzene
- Complex Cyanides
- Creosote
- Hydrazine Compounds
- Isopropanol
- MEK
- MIBK
- Methylene Chloride
- PCB's
- Pentachlorophenols
- Pesticides
- Phenol
- RDX
- TNT
- Toluene
- Xylene
- Polynitrophenols

TABLE 3

Groundwaters containing:

- BTX
- Creosote
- 1,2 DCA
- DCEE
- Dioxins
- Dioxanes
- Freon 113
- $MeCl_2$
- MIBK
- PCBs
- PCE
- Pentachlorophenol
- bis (2-chloroethyl) ether
- Pesticides
- Polynuclear Aromatics
- 1,1,1 TCA
- TCE
- THF
- Vinyl Chloride
- Triglycol dichloride ether

TABLE 4

TREATABILITY AND DESIGN STUDY RESULTS USING PILOT PLANTS ON SITE

Customer	Application	Contaminants	Results
Bulk Chemical Transfer Depot	Contaminated groundwater	TCE, PCE, methylene chloride	Water treated and reinjected into ground
Municipal Water Producers	Contaminated drinking water supply	TCE, PCE, color	VOCs and color reduced to below state action levels
Aerospace Co.	Paint stripping wastewater	Methylene chloride	$MeCl_2$ reduced from 4000 ppm to less than 100 ppb
Chemical Co.	Wastewater	Misc. pesticides (including DBCP)	DBCP and other pesticides reduced to less than 1 ppb
Automotive Co.	Groundwater	TCE, $MeCl_2$	Reduced 10 ppm to 5.0 ppb
Electronics Co.	Wastewater/runoff water, groundwater	PCBs, ViCl, DCA + other VOCs	Reduced PCBs to less than 1 ppb; VOCs reduced to below state action levels
Munition Plants	Wastewater	TNT, RDX	TNT & RDX reduced from 100 ppm to less than 1 ppm
Army Bases	Contaminated groundwater	DIMP, DBCD, VOCs	DIMP & DBCD reduced to less than 10 ppb; VOCs reduced to below state action levels
Semiconductor Co.	Wastewater	EDTA	Reduced EDTA from 6,000 ppm to 100 ppm (acceptable discharge standard)
Petrochemical Mfr.	Wastewater	Benzene	Reduced benzene from 10 ppm 50 ppb
Semiconductor Mfr.	Groundwater	benzene, toluene, xylene, ethyl benzene	Reduced contaminants from 14.0 ppm to 4.0 ppb

TABLE 5

FULL-SCALE ULTROX® SYSTEMS

Customer	Application	Contaminants	Results
Wood Treating Plants (2)	Wood treating wastewater	Phenol, pentachlorophenol	Water treated and discharged to POTW
Closed Wood Treating Plant	Contaminated groundwater	Phenol, pentachlorophenol	Water treated and discharged to POTW
Chemical Plant	Fume scrubbing water	Hydrazine, monomethyl hydrazine, unsymmetrical dimethyl hydrazine	Destroyed parent compounds to N.D. levels and dimethyl nitrosamine below 10 ppb
Automotive Foundry	Contaminated groundwater	TCE, Trans 1,2-DCE	Water treated and discharged to lake
Aerospace Co.	Contaminated groundwater	TCE, TCA, DCA, PCE $MeCl_2$, vinyl chloride	Water treated and discharged to POTW
Chemical Plant	Wastewater	Phenol, formaldehyde	Water treated and discharged to POTW
Semiconductor Co.	Contaminated groundwater	THF	Replaced a GAC system to reduce THF from 1,000 ppb to less than 5 ppb

TABLE 6

TYPICAL DIRECT OPERATING & MAINTENANCE COSTS USING UV-OXIDATION FOR WATER SUPPLIES*

Type of Water	Contaminants	Total Contaminant Concentration	Treatment Standards	Direct O & M Cost Range ($/1000 gal)
Contaminated potable drinking groundwater	TCE, PCE	less than 20 ppb	Drinking Water	0.10 to 0.20
Contaminated potable drinking groundwater	TCE, PCE	200 ppb	Drinking Water	0.20 to 0.30
Contaminated potable drinking groundwater	Color	70 color units	Drinking Water	0.10 to 0.15

* Assumes cost of electrical energy is $0.06/KWH

TABLE 7

DIRECT OPERATING & MAINTENANCE COSTS FOR UV-OXIDATION AT INDUSTRIAL INSTALLATIONS

Type of Water	Contaminants	Contaminant Concentration	Discharge to	Volume Treated Per Day	Direct O & M Cost Range
Wood Treating Wastewater	Pentachlorophenol and phenol	150 ppm	POTW	30,000	\$1.25-1.35/1000 gal
Wood Treating Groundwater	Pentachlorophenol and phenol	5 ppm	POTW	86,400	\$0.90-\$1.00/1000 gal
Fume Scrubber Water	Hydrazene, Monomethylhydrazine Unsymmetrical-dimethylhydrazine	5,000 ppm	Biotreatment Plant On-Site	600 - 1500	\$0.086/gal
Contaminated Groundwater	TCE, trans DCE $MeCl_2$	5 ppm	Surface Water	300,000	\$0.47/1000 gal
Contaminated Groundwater	TCE, TCA, DCA, PCE, $MeCl_2$ ViCl	600 ppb	POTW	72,000	\$0.33/1000 gal
Contaminated Groundwater	THF	1 ppm	Ground	216,000	\$0.39/1000 gal
Wastewater	Phenol	90 ppm	POTW	4,300	\$6.48/1000 gal

TABLE 8

TYPICAL CAPITAL COSTS FOR UV-OXIDATION SYSTEMS

Type of Water	Contaminants	Total Contaminant Concentration	Water Flow Rate (GPD)	Price Range (uninstalled) $
Wood Treating Wastewater	Pentachlorophenol Phenol	150 ppm	30,000	125,000-150,000
Wood Treating Groundwater	Pentachlorophenol Phenol	5 ppm	86,400	175,000-200,000
Fume Scrubber Water	Hydrazines	5,000 ppm	600-1500	125,000-150,000
Contaminated Groundwater	TCE, trans DCE $MeCl_2$	5 ppm	300,000	225,000-275,000
Contaminated Groundwater	TCE, TCA, DCA PCE, $MeCl_2$, ViCl	600 ppb	72,000	130,000-150,000
Contaminated Groundwater	THF	1 ppm	216,000	250,000-300,000
Wastewater	Phenol	90 ppm	4,300	45,000-55,000

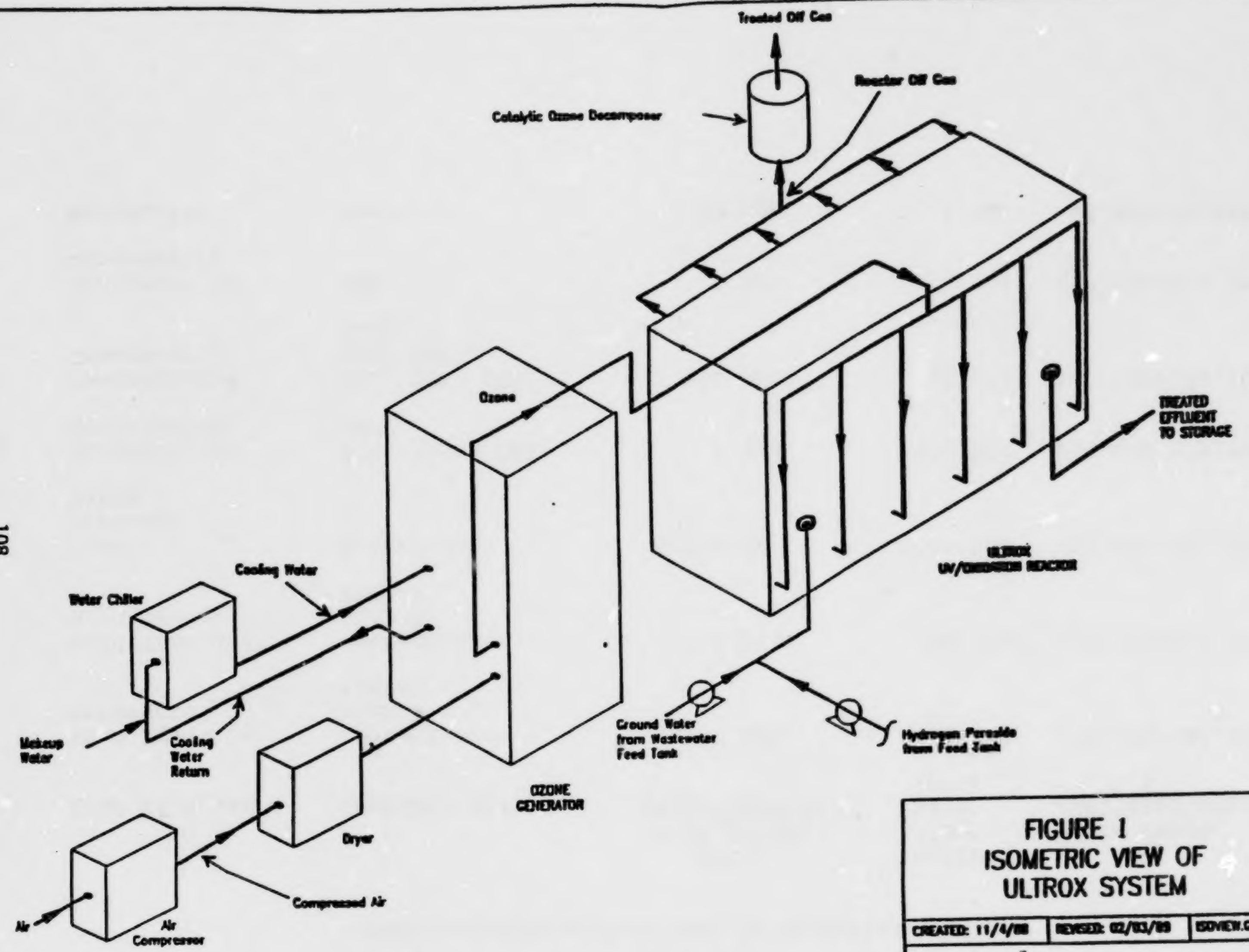
Treated Off Gas
Reactor Off Gas
Catalytic Ozone Decomposer
Ozone
TREATED EFFLUENT TO STORAGE
ULTROX UV/OXIDATION REACTOR
Cooling Water
Water Chiller
Makeup Water
Cooling Water Return
Ground Water from Wastewater Feed Tank
Hydrogen Peroxide from Feed Tank
OZONE GENERATOR
Dryer
Compressed Air
Air
Air Compressor

FIGURE 1
ISOMETRIC VIEW OF
ULTROX SYSTEM

CREATED: 11/4/88 | REVISED: 02/03/89 | ISOVIEW.CRF

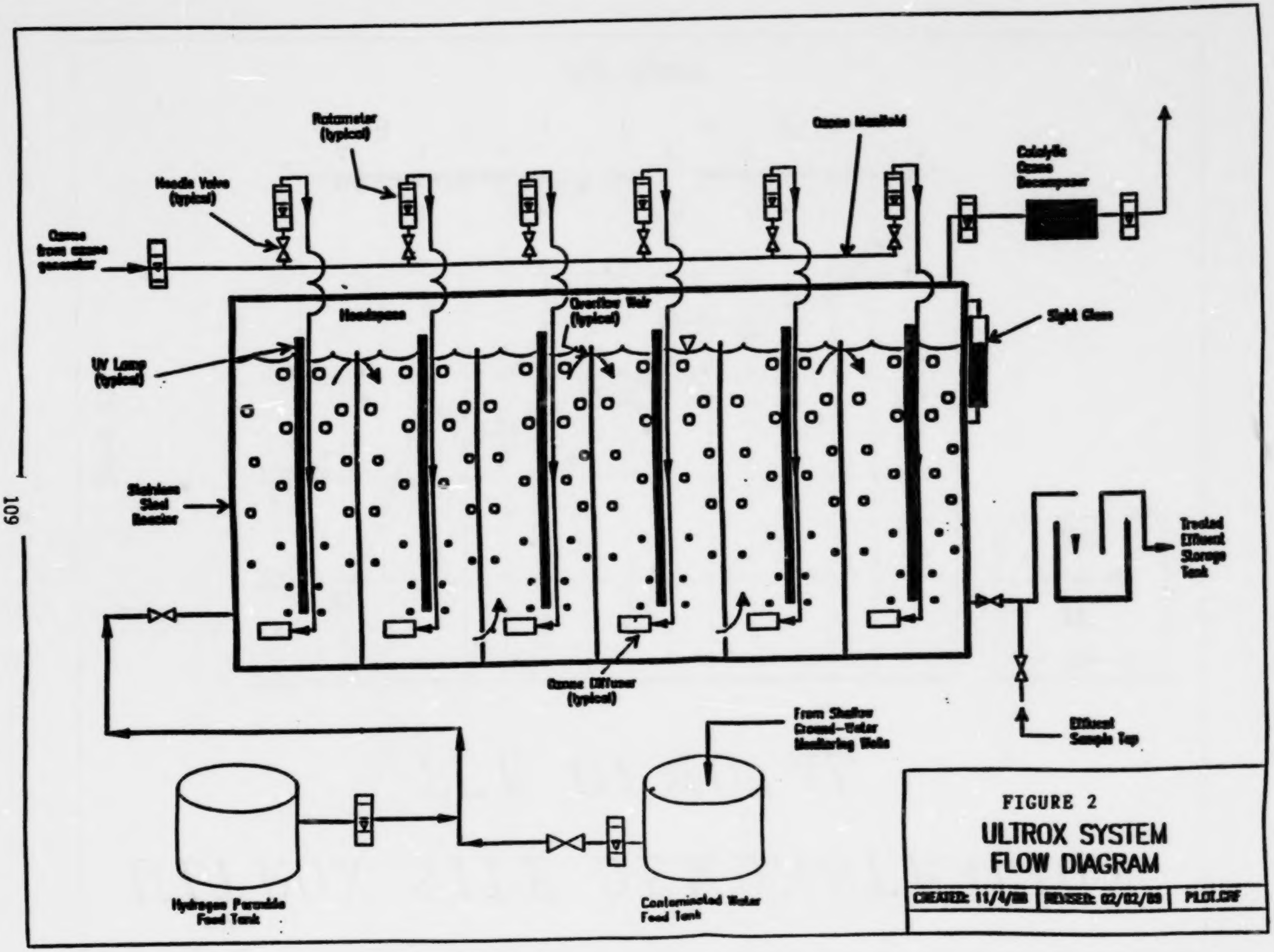
Rotameter (typical)
Ozone Manifold
Needle Valve (typical)
Catalytic Ozone Decompressor
Ozone from ozone generator
Headspace
Overflow Weir (typical)
Sight Glass
UV Lamp (typical)
Stainless Steel Reactor
Treated Effluent Storage Tank
Ozone Diffuser (typical)
From Shallow Ground-Water Monitoring Wells
Effluent Sample Tap
Hydrogen Peroxide Feed Tank
Contaminated Water Feed Tank
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FIGURE 2
ULTROX SYSTEM
FLOW DIAGRAM

FIGURE 3

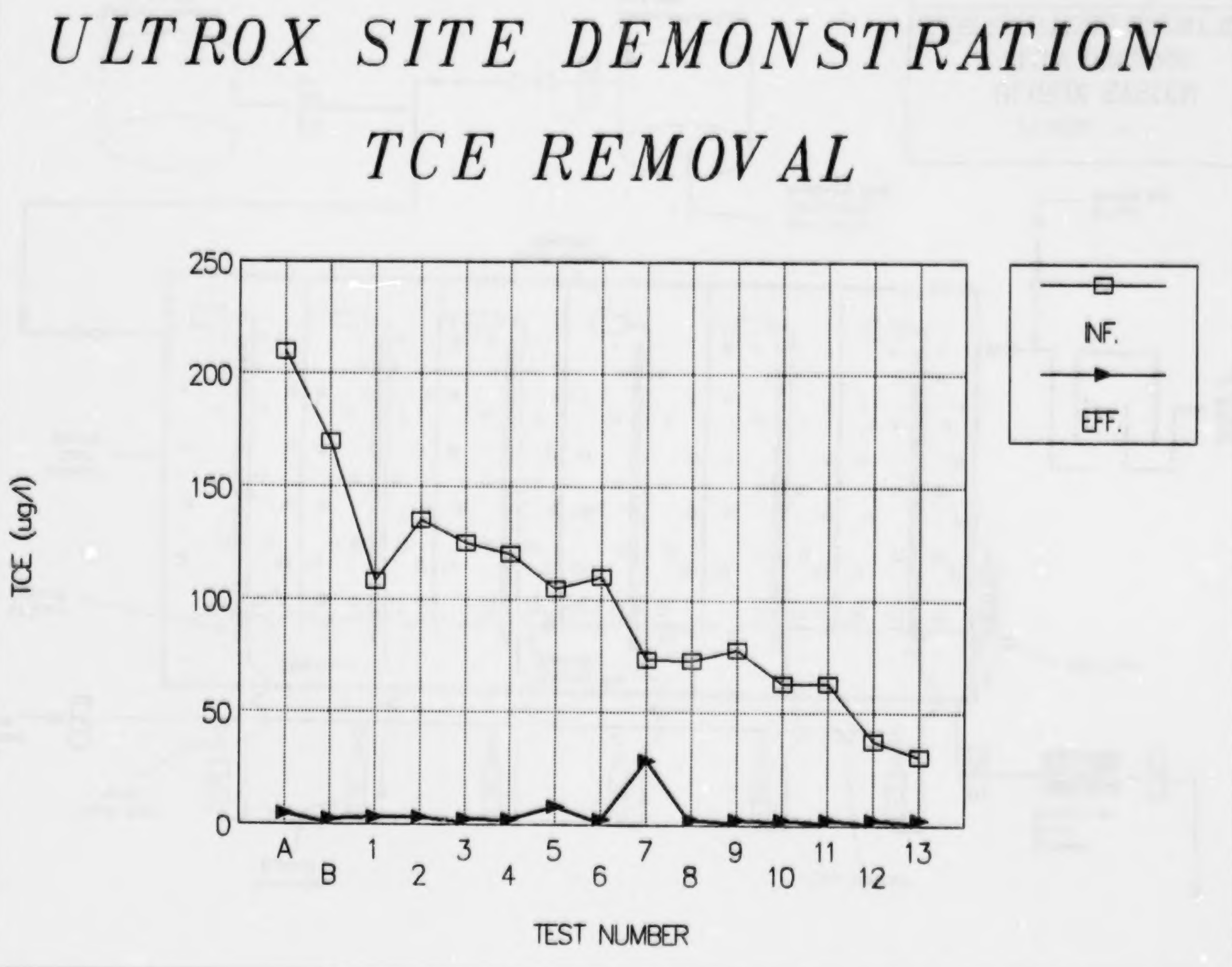

ULTROX SITE DEMONSTRATION
TCE REMOVAL
TCE (ug/l)
250
200
150
100
50
0
A
B
1
2
3
4
5
6
7
8
9
10
11
12
13
TEST NUMBER
INF.
EFF.

FIGURE 4

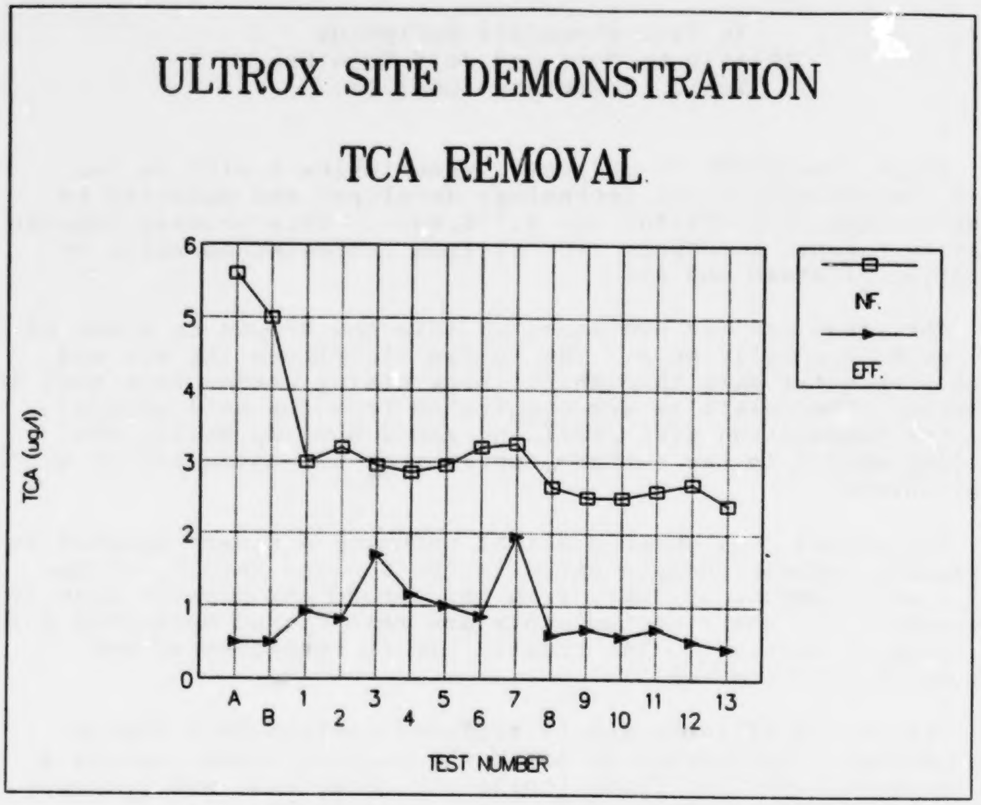
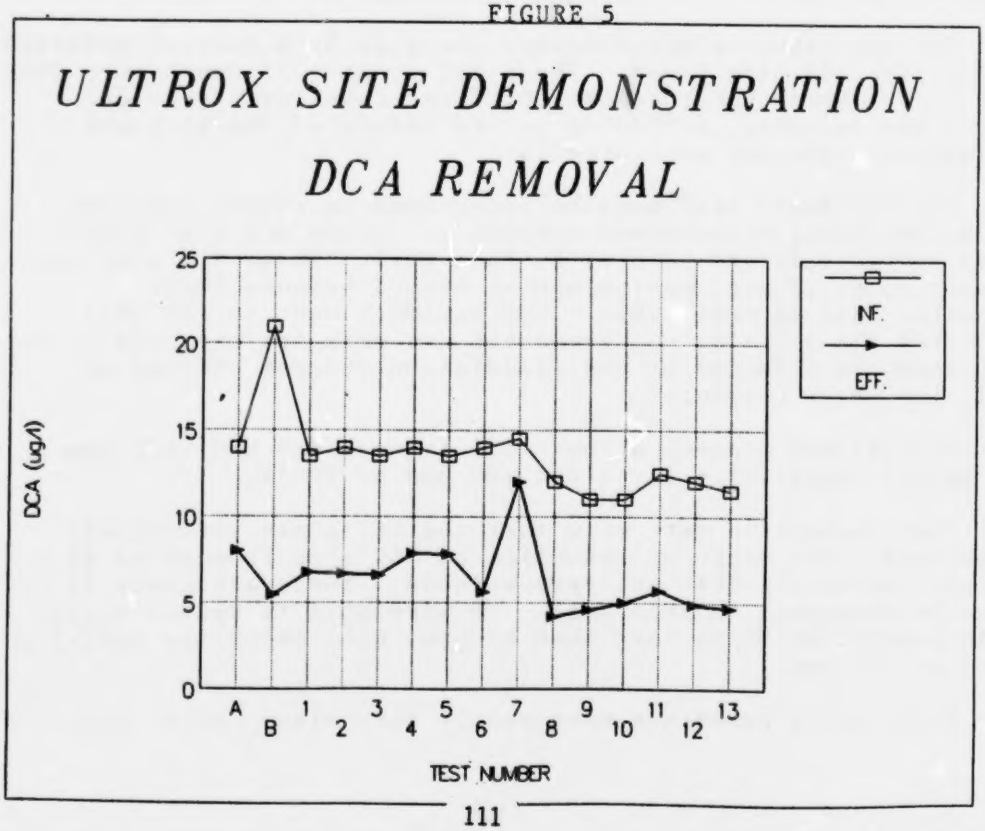


FIGURE 5



In Situ Steam/Air Stripping

Phillip La Mori and Jeff Guenther
Toxic Treatments (USA) Inc.

Toxic Treatments is currently remediating a site in San Pedro, California, using technology developed and patented by Frank Manchak (U.S. Patent No. 4,776,409.) This process removes volatile organic compounds (VOC's) from contaminated soils by injection of steam and air.

The steam and air are injected into the ground by means of a pair of hollow kelly bars. The kellys distribute the air and steam within the soil through rotating mixing blades five feet in diameter. The volatiles are evaporated from the soil matrix, into the remediation air. Effluent gases move up beside the drilling shafts to the surface, where they are collected in a metal shroud.

The shroud runs under a slight vacuum. A blower mounted on a separate process chassis extracts the air and vapors, along with a small amount of dust, from the shroud and directs them to a process train where contaminants are removed and collected for recycling or disposal. The treated air is recompressed and reinjected into the soil.

The shroud effluent gas is analyzed continuously during remediation. Instruments on board the process train include a gas chromatograph, two flame ionization detectors, and pressure, temperature, and humidity measuring equipment.

The apparatus is moved around the site by a heavily modified Caterpillar 583 pipe layer. The drill stems will reach more than thirty feet below the surface. Drilling rates of 3 feet per minute are possible, depending on the nature of the soil and contaminant type and concentration.

The San Pedro site must be remediated to remove residual VOC's, including chlorinated compounds. There are also semi-volatile hydrocarbons (SVH's) in this soil. These SVH's do not present much, if any, environmental hazard because their migration rate is negligible. You wouldn't want to eat this soil, but the SVH's do not evaporate and were not expected to be significantly affected by the remediation process because of their low vapor pressures.

Initial VOC concentrations were between 824 and 1872 ppm. The target remediation level was 100 ppm of VOC's.

Test results to date show that the VOC's are effectively remediated. The range of reduction of VOC's is from 96 to 99 percent, using EPA 8240 analysis methods. There are about 15 volatile compounds in this soil. We were able to reduce their total concentration to less than 55 ppm, well below the target level of 100 ppm.

Silty soils remediate more easily than clay. Moist clay soils containing tetrachloroethylene were also remediated by better than 95 percent, but the final levels were 53 to 203 ppm, somewhat higher than target levels. This may be adequate, but changes have been made in the process which improved the absolute remediation level.

The process also removed most of the semivolatiles as listed in EPA 8270. This was somewhat unexpected and we have spent considerable time trying to determine the mechanism for their removal. About 85 percent of the SVC's found on the site are phthalate esters of various aliphatic radicals, e.g., ethylhexyl phthalate. We believe that these esters are being hydrolyzed to an intermediate acid salt and an alcohol. The alcohol appears to dehydrate to an olefin. Soil and recovered fluid analyses support these ideas. Some SVC's like isophorone and phenol may be quantitatively removed by steam distillation or vaporization.

The recovered VOC's represent most of the starting calculated mass. Field monitoring of gases outside the shroud and analyses of adjacent blocks show little or no escape of VOC's to the surroundings. We believe that the process is very effective for volatile materials. The process also is somewhat effective for semi-volatiles, but this depends on the species present.

Treatment rates vary depending on the amount of contaminants and type of soil, as indicated above, but the average is about 6 to 8 cubic yards per hour.

The Detoxifier (tm) apparatus may also be used for other types of in situ treatment, including the addition of soil stabilizers, injection of reagents, or for bioremediation. Two more complete drilling units have been assembled, and process trains for those units will be designed to match the needs of particular applications.

AVERAGE VOC CONCENTRATION
(ppm)

Area	Before	After
A	1,114	12
B	1,353	30
D	3,954	139

AVERAGE SVH CONCENTRATION
(ppm)

Area	Before	After
A	3,775	627
B	12,116	1,766
D	1,014	85

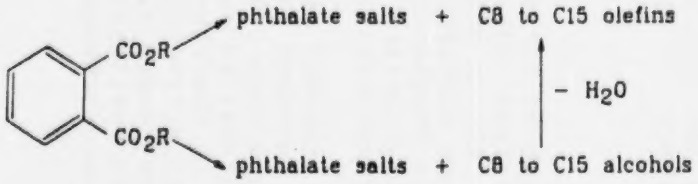
VOC CONCENTRATIONS (ppm)

Block	Before	After	% Reduction
A-8-g	1,149	18	98
A-9-g	824	7	99
A-10-g	1,368	11	99
B-50-n	1,123	23	98
B-51-n	1,500	13	99
B-51-m	1,872	65	97
B-52-m	917	29	97
D-92-b	2,305	53	98
D-93-b	3,720	163	96
D-94-b	5,838	203	97

SVH CONCENTRATIONS (ppm)

Block	Before	After	% Reduction
A-8-g	1,794	637	64
A-9-g	2,510	653	74
A-10-g	7,020	592	92
B-50-n	22,829	1,670	93
B-51-n	14,924	2,304	85
B-51-m	10,040	2,496	75
B-52-m	669	594	11
D-92-b	707	55	92
D-93-b	1,465	90	94
D-94-b	869	111	87

FATE OF SEMIVOLATILE COMPOUNDS


CO2R
CO2R
phthalate salts + C8 to C15 olefins
– H2O
phthalate salts + C8 to C15 alcohols

1032 lbs. of bis-2-ethylhexyl phthalate produce 296 lbs. of C_8H_{16}

FATE OF SEMI-VOLATILE COMPOUNDS

Compound	Pretreatment Amount (lbs)	Percent	Recovered Amount (lbs)*	Percent
bis-2-ethylhexyl phthalate	424.4	38	0	0
butyl cellosolve	13.1	1	9	2
isophorone	3.8	<1	28	6
2 ethylhexyl adipate	2.0	<1	0	0
phthalate matrix	607.6	55	0	0
glycol ethers	11.8	1	<1	0
C8-C15 HC	34.1	3	393	83
others	7.5	<1	42	9
Total	1104.5	100 ±	473	100
	10 Block		Total Project	

VOC MASS BALANCE

Treatment Blocks Remediated	Pounds Recovered	Pounds Removed	% VOC Recovered
6	124.5	142.5	87.4
10	264.8	296.6	89.3

THC CONCENTRATIONS (ppm)

Block	Before	After	% Reduction
A-8-g	2,943	655	78
A-9-g	3,334	660	80
A-10-g	8,388	603	93
B-60-n	23,952	1,693	93
B-51-n	16,424	2,317	86
B-61-m	11,912	2,550	79
B-62-m	1,588	623	61
D-92-b	3,012	108	96
D-93-b	5,184	253	95
D-94-b	6,707	314	95

THE PIEPHO CORPORATION
9341 Cornwell Farm Rd. Great Falls, Va. 22066, (703) 759-7074

INTRODUCTION

Ralf F. Piepho Abwassertechnik GMBH has been in the waste water treatment business in West Germany for ten years. We are located in Bredenbeck, a small village just outside of the city of Hannover. Over the years, our customers have ranged in size from extremely large concerns, such as the German Navy and VW to small, single factory furniture and textile companies. Our latest project is cleaning the runoff/leachate from a large landfill for the government of East Germany.

Our firm is relatively small. We only have about 25 employees. However, over the last few years we have developed a partnership with Rhein Braun, one of the largest energy firms in Germany. This partnership, called Union Piepho, gives us the facilities and resources to handle jobs of any size. We have also developed partners in a number of other countries including Italy, Denmark, India, and the United States.

PROCESS DESCRIPTION

We have developed a chemical-physical process for the treatment of waste water. This process consists of Reaction Separation Agents NT75 and Piepho treatment machines.

Reaction Separation Agent NT75

NT75 is a separating reactant on a clay basis which by virtue of its extraordinarily high effectiveness can crack emulsions, adsorb contaminants, flocculate and finally encapsulate, all in one process stage. Furthermore, once the contaminants have been encapsulated, the resulting sludge will no longer leach. Due to this characteristic, we have been able to dispose of much of our sludge on standard household dumps, thus reducing the total treatment costs dramatically.

The clays in Reaction Separation Agent NT 75 are minerals with an expandable triple layer arrangement and a cation exchange capacity of 80 - 100 m/100g. The grain size distribution ranges from 0.5 - 1.5. The use of bentonite as the main flocculant is unusual because the particles are too small to give good adsorption. On the other hand the negative charge on its surface causes it to be attracted to cationic positive polymers. When the polymers have bonded all oil molecules the polymer oil complexes created become positively charged and coated by particles of clay. The bentonite then exchanges ions for polymer oil complexes.

The release of clay particles from this bond is virtually excluded. A polymer oil complex coated by clay particles is practically cocooned - it is fixed and the reverse reaction or breakdown is not possible, even if the pH value changes, thus giving us our stable sludge. Also, the stabilization and encapsulization process of the sludge doesn't stop but continues even after dumping and as such increases the resistivity to leaching.

One must bear in mind that the interaction between polymers and clay particles starts immediately after input of the additive into the waste water, and continues during the adsorption process. The slightly reduced effectiveness of the polymers is balanced by an increase in flocculaton, typical for clay additives.

This possibility, to control polymer oil complexes at the point of their reaction and formation, is created by combining all chemicals required in the water treatment into one formula. The prerequisite for this is to prepare (isolate) those components capable of changing the pH value such that they become effective at the right point in time and in the right sequence - so raising or lowering the pH value.

The use of specially treated organic acids and alkalis with different solubilities allows the pH value to be controlled and determined throughout the process.

A condition of the treatment with reaction separation agent NT75 is that the fine-grain powdered product is well mixed into the waste water. During this mixing process the polymers are distributed, the acids and alkalis dissolve, polymer oil complexes are formed - which are immediately cocooned by the clay particles and so encapsulated. This process is repeated continuously during the reaction until all oil and other contaminants are fixed. The mixing may then be terminated and conventional sedimentation and drying of the sludge follows. The time period required in the treatment module of the plant depends on the waste water - but it is usually about 5 minutes; the same applies to the sedimentation phase.

Piepho Wastewater Treatment Machines

The Piepho treatment machines perform 5 basic functions.

1) Automatic addition of Reaction Separation Agent NT75
2) High speed mixing of the NT75 into the waste water
3) Sedimentation
4) Filtration
5) Drying,removal of the sludge

The machines have been designed to be fully automatic, but can also be run manually. Many of our machines process in batches, while others can clean continuously. The capacities of the machines range from 400 l/h to 30,000 l/h, and because they are fully automatic, they can be run in excess of 20 hours a day, thus allowing our largest machine to clean 600,000 liters in a single day. Also, the machines have been designed to fit into containers which allow for easy transportation and single day setup.

TYPE OF CONTAMINANTS TREATED BY THE PIEPHO SYSTEM

In the past, using the Piepho process and other processes which can be integrated into our system (reverse osmosis, biological treatment, etc.), we have been able to handle all pollutants we have come across in water. The Piepho process itself is most effective at removing water-insoluble pollutants, both organic and inorganic. It has also been effective at removing a variety of dissolved organics and inorganics (through the addition of both our patented reaction separation agent NT 75 and active carbon), and heavy metals.

In Europe, we have concentrated on the handling of industrial waste water, polluted groundwater, and landfill leachate. Most frequently, these applications lead us to a waste water contaminated with oil bearing emulsions, chlorinated hydrocarbons, heavy metals, and paint remainders.

We feel that our system has the capacity to clean any waste water. Whether or not our process is economically efficient in its treatment of a specific waste water must be tested in our laboratory. For some industrial firms who generate small quantities of very complicated waste water, it may still be more cost efficient to have their water hauled away to a large waste water treatment plant.

QUALITY OF EFFLUENT ACHIEVED WITH THE PIEPHO SYSTEM

Our process is very flexible with respect to the achievement of desired clean-up levels. The quality of the treated water can be increased through the addition of chemicals, or through the choice of processes to be used in the treatment system. The best way of illustrating this is with examples.

Example 1

For the continuous circulating process water in the finishing industry, it only makes sense to clean the water to the level where it meets the quality demands for its continued use. In cases such as these, single stage systems are usually all that is necessary.

Example 2

If the treated waste water will be removed to a community biological treatment plant, then it must only be cleaned to the level of the inlet values for the plant. In most cases, this can also be handled by a single stage process.

Example 3

If higher quality is needed, for example, if the water will be discharged directly into surface waters, or if total quality levels or single parameters correspond to those of drinking water, our process can also be used to meet these demands. The cost would increase (depending, of course, on the quality of the waste water before treatment), and many stages may be needed, including:

Pretreatment
- (1) Prescreening to remove suspended solids
- (2) Pretreatment to remove lower density materials (If the water contains more than 2% oil,fats,etc., this pretreatment will make the next stages more efficient)

Piepho Treatment
- (1) First stage - addition of NT 75, a fatty acid, bentonite based coagulent/flocculent.
- (2) Second stage - addition of active carbon
- (3) Third stage - addition of Fuller's earth mixture
- (4) Fourth stage - removal of 2,3 above by NT 75

Further treatment

If necessary, further stages can be integrated into the Piepho system. These would include extra filters, reverse osmosis, membrane filtration, etc.

To this date, we have been able to meet all quality demands that have confronted us.

LIMITATIONS OF THE PROCESS

The limitations of our process are accounted for by our pretreatment stages. Our process is not effective if the water contains solids and coarse materials. Therefore, these must be removed as much as is mechanically possible in the pretreatment. Also, it is not economical to use NT75 to treat low density material, such as oil and grease. Because of this, we have developed our own pretreatment to recover these materials. Our process is especially good at dealing with high concentrations of contaminants. However, if the concentrations are too high (above 2%), then the water must be diluted. The limitation here is mechanical. The machines are not designed to handle large amounts of sludge. Mr. Piepho's suggestion in cases where the concentration is too high is to use the water which has already been treated to dilute the remaining waste water. In this way only a minimal amount of fresh water must be used.

COST

General statements about the economic side of our process are difficult to make. Exact costs for the system will depend on the type of contaminants in the waste water to be cleaned, the concentration of these contaminants, and the quality level of cleaning which is desired. The fixed costs, i.e. the cost of the machine(s) can range from 21,000 DM for a single stage machine with a capacity of 300 liters per hour, to 750,000 DM for a multi-stage system with a capacity of 25,000 l/h. The treatment costs are even harder to generalize. They range from 0.3 - 3 cents per gallon if only a single stage treatment is required, to 2 - 10c/g for water requiring multi-stage treatment. However, most waste waters require in the range of 2 - 5 c/g for cleaning. Examples may be helpful:

Single Stage Treatment

Single stage treatment consists of a single Peipho machine, with capacities ranging from 300 l/h to 25,000 l/h, and the appropriate mixture of chemicals. This is researched by our laboratory for the particular water to be cleaned. The water is pumped into the machine where the chemicals are added and mixed with the water at high speeds, allowing coagulation/flocculation to take place. This water is then moved into the sedimentation tank where the sludge is removed automatically by a filter band. The water must pass through a filter before it is discharged. The result is a treated water and a sludge which has encapsulated the contaminants and which, according to the "Wehrwissenschaftliches Institut fur Material Untersuchung" (State Scientific Institute for Material Study), was not susceptible to leaching over the term of a one year study using distilled water and a sludge contaminated with hydrocarbons.

Costs: The costs for a single stage system are as follows.

Machine: 21,000 - 300,000 DM
Chemicals - Generally 0.5 - 3.5 kg are used per 1000 liters.
1 kg costs 3 DM

Treatment costs are therefore 1.5 - 10.5 DM per 1000 liters or 0.3 to 2 cents per gallon.

Other costs such as electricity, labor, and filter paper are insignificant.

Multi-stage Treatment

The full treatment offered would consist of the following.

1) Pretreatment - Skimming off of low density materials. Screening of solids.
2) Stage 1 - Same as a one stage treatment. Just a single machine and the addition of NT 75.
3) Stage 2 - A tank and a mixing turbine for the addition of activated carbon.
4) Stage 3 - The same setup as stage 3, only here it is for the addition of a special Fuller's earth mixture.
5) Stage 4 - A machine exactly like that in stage one. Here NT 75 is used to coagulate the pollutant loaded absorbents from stages 2 and 3.
6) Stage 5 - In exceptional cases, a membrane process or a biological reactor can be integrated into the Piepho process.

Fixed Costs:

Pretreatment - oil skimmer		6000 DM
solid screening process -		market price
Machines - 2 are needed (stages 1 and 4)		20,000 to 300,000 DM each
Mixing tanks - (2)	approx.	30,000 to 50,000 DM each

Additional treatment - Membrane or biological reactor market price

Total cost - approx. 100,000 to 750,000 DM - this does not include additional treatment

Treatment Costs: (per 1000 liters)

Pretreatment - liquid separation agent (3 DM/l)	= 3 DM
Stage 1 - NT 75 (0.5 - 3.5kg at 3 DM per kg)	= 1.5 - 10.5 DM
Stage 2 - Active carbon (0.5 - 3 kg at 5 DM/kg)	= 2.5 - 15 DM
Stage 3 - Fuller's earth mixture(0.5-3.5* 3DM/kg)	= 1.5 - 10.5 DM
Stage 4 - NT 75 (0.5 -3.5 kg)	= 1.5 - 10.5 DM
Total	= 10 - 49.5 DM
	or 2 to 10 cents per gallon

POSSIBLE USES OF THE PIEPHO PROCESS IN THE U.S.

We see three areas where our process could be used in the U.S.

1) To clean contaiminated water at its source of contamination; i.e. sales to industry. This is the area where we have been most successful in Europe. Our range of products allow us to treat a wide variety of wastewater streams.

2) Cleaning contaminated groundwater and surface waters, under Superfund and other similar state laws. We have had plenty of experience in these areas in Europe and our products are well suited for this type of use.

3) Using our technology as part of a larger process to clean contaminated soil. We have found two ways in which this can be done.

a) Using our process in conjunction with a mobile soil washing plant. This plant uses specially pretreated water to wash the contaminants from the soil. The contaminants end up in the washing water and are removed using the Piepho process. Plants of this type will soon be in production in Europe.

b) Using our technology as part of an in situ soil flushing process. In this case we would force specially treated water through the contaminated soil. The water would pick up the contaminants as it flushed through the soil. This process would be repeated until the required levels of contamination had been reached or until the water could no longer remove any contaminants from the soil.

REGIONAL BIOLOGICAL DECONTAMINATION CENTERS FOR THE CLEAN-UP OF CONTAMINATED SOIL, SLUDGES AND INDUSTRIAL WASTE-WATERS

A PRESENTATION FOR THE
EPA-FORUM ON INNOVATIVE TREATMENT TECHNOLOGIES: DOMESTIC AND
INTERNATIONAL, ATLANTA, JUNE 20 - 22, 1989

BY

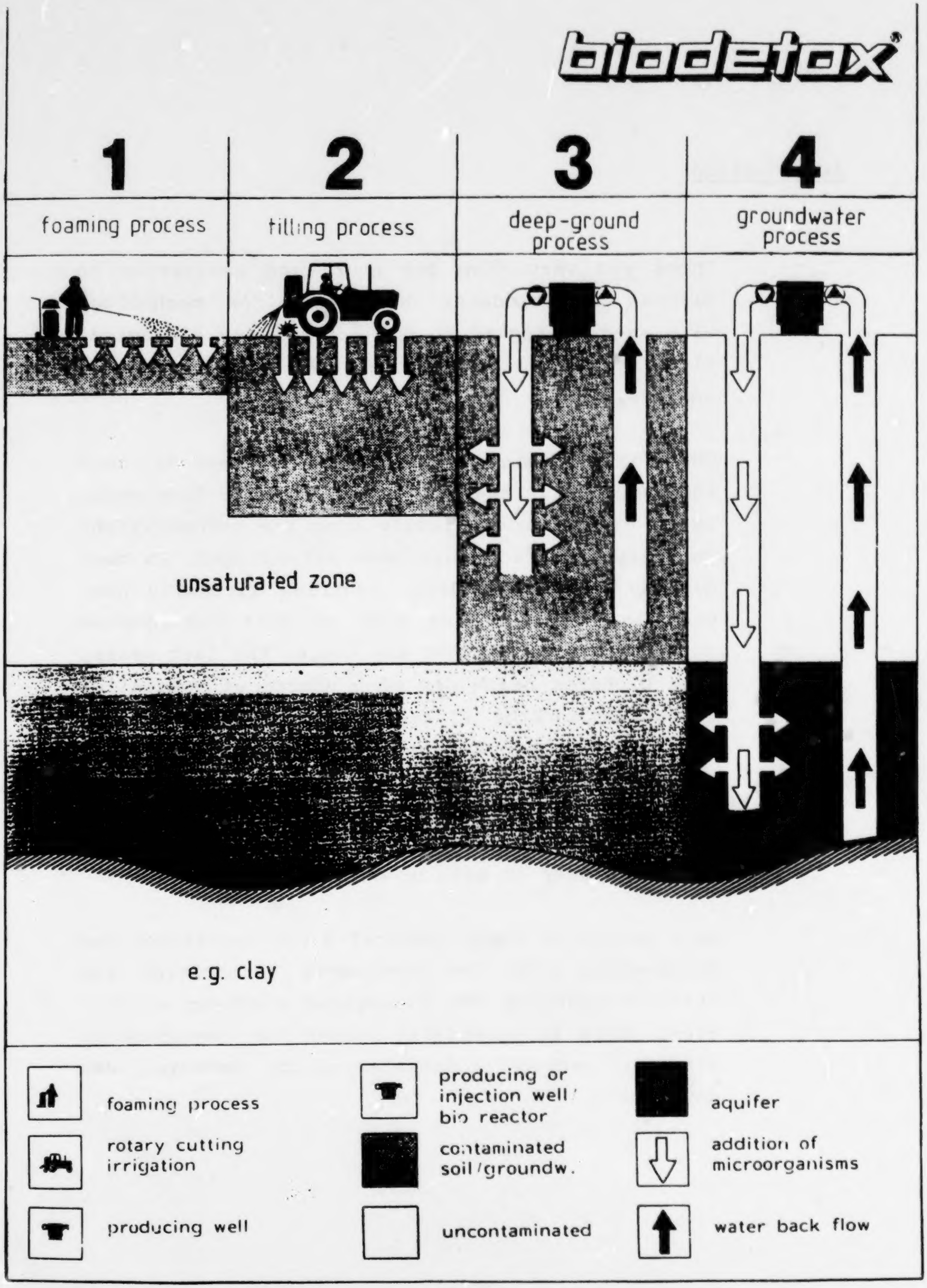
DR. HEIN KROOS, PRESIDENT AND GENERAL MANAGER,
BIODETOX GMBH, 3061 AHNSEN, WEST GERMANY

Introduction

Thank you very much for your kind invitation to discuss the biodetox decontamination technology with special regard to our concept for biological clean-up activities in regional decontamination centers.

There is sufficient scientific proof that oil contaminated soils and sludges can more or less easily be cleaned biologically once the preconditions for biodegradation have been established. In West Germany and surrounding countries virtually hundreds of thousands of tons of oil contaminated soils were cleaned that way during the last years, with biodetox being one of a number of specialist companies working since 1981 in this field and offering a broad range of services including field expertise, analytics, hazard evaluation and special decontamination services based on various patented biological clean-up processes which can be used either in situ or on site.

As a result of these years of field experience and discussions with the regulatory authorities the "Bio-Pit"-process for biological clean-up activities, which is especially suited for temporary on site or permanent decontamination centers, was developed.


biodetox
1
foaming process
2
tilling process
3
deep-ground process
4
groundwater process
unsaturated zone
e.g. clay
foaming process
rotary cutting irrigation
producing well
producing or injection well / bio reactor
contaminated soil / groundw.
uncontaminated
aquifer
addition of microorganisms
water back flow

Special purpose of this presentation is to demonstrate this proven process which has been equally accepted by the German Federal and State Authorities as well as by the public including the neighbouring communities. This process is presently running successfully in a number of German regional decontamination centers combining regional private initiative with the central R & D-quality control and marketing facilities of a nationwide franchise system. The process is economically feasible, without receiving government or state subsidies whatsoever.

The biodetox Bio-Pit process consists of following steps:

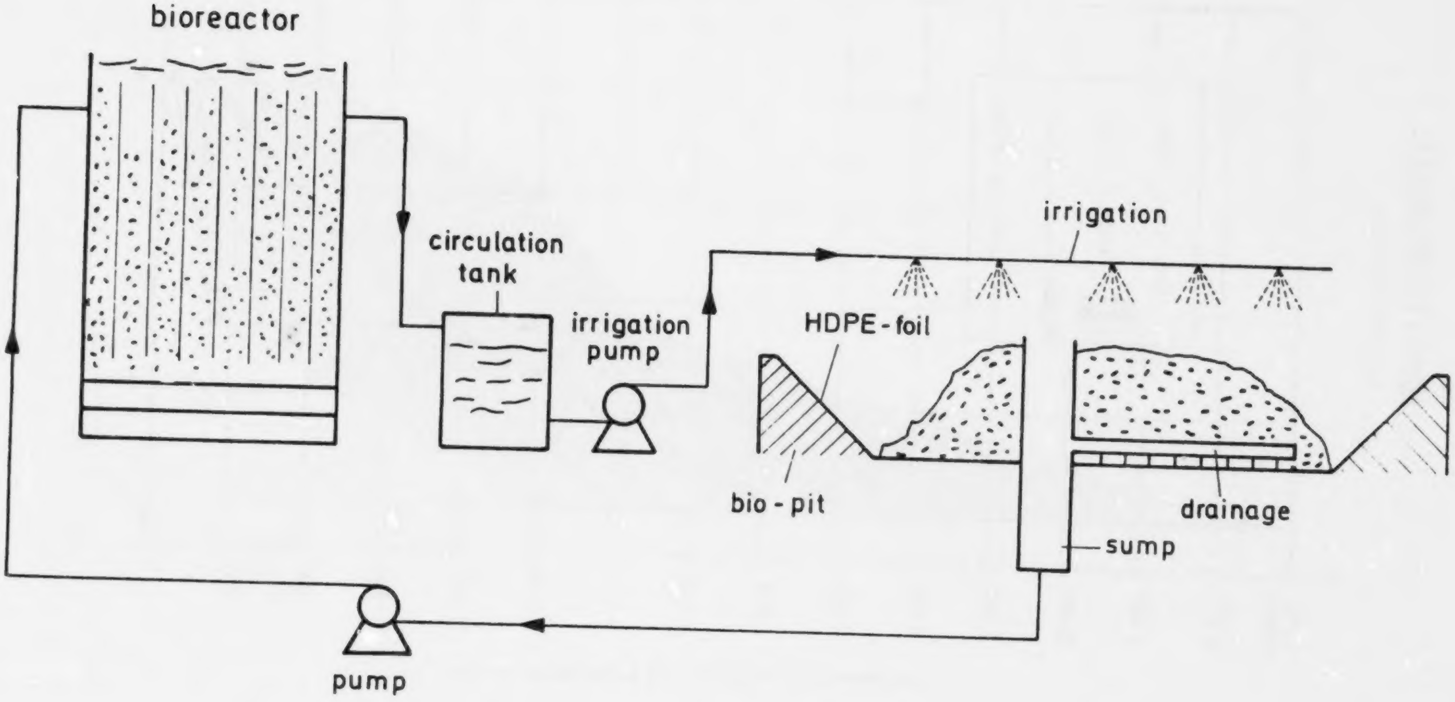
Contaminated soil is transported to high density polyethylene treatment beds and receives on arrival a pre-inocculation with the appropriate microorganism cultures (biofoaming). Water is then sprayed over the treatment bed, percolating down to a drainage system which leads to a collection sump and is then pumped to an aerobic bioreactor. The bioreactor is filled with fixed, vertical sheets or other filling material, on which biomass either especially cultivated for this purpose or as a standard mixed culture grows. The reactor is aerated at a rate of 4 m^3 per m^3 reactor-volume per hour and has a hydraulic rentention time of 6 - 12 hours. There the dissolved pollutants are finally degraded should that not have happened in the soil already. Therefore, we have clean-up activities at two stages: First in the soil itself (the problematical blackbox!), and then in the reactor with its more homogeneous medium, especially suited for biodegradation. The cleaned water passes into a transit tank where nutrients and additional biomass can be added as required. The water is then pumped to the treatment bed via the irrigation sprays establishing a closed loop system.

The following schematic illustration of the Bio-Pit process will demonstrate these details more clearly. Initially, only soil contaminated with mineral oil products such as gasoline, kerosene, diesel fuel, motor oil, lubricants and heating oil were treated in bio-pits. Meanwhile a broad range of other pollutants can be treated successfully including light aromatic compounds such as benzene, toluene, xylene, styrene, cresol, phenol and phenolic compounds plus the so called coal tar constituents (PAH).

Degradation time for oil contaminated soil has been found to be between 6 to 12 weeks on the average. The following degradation diagrams will show some average values.

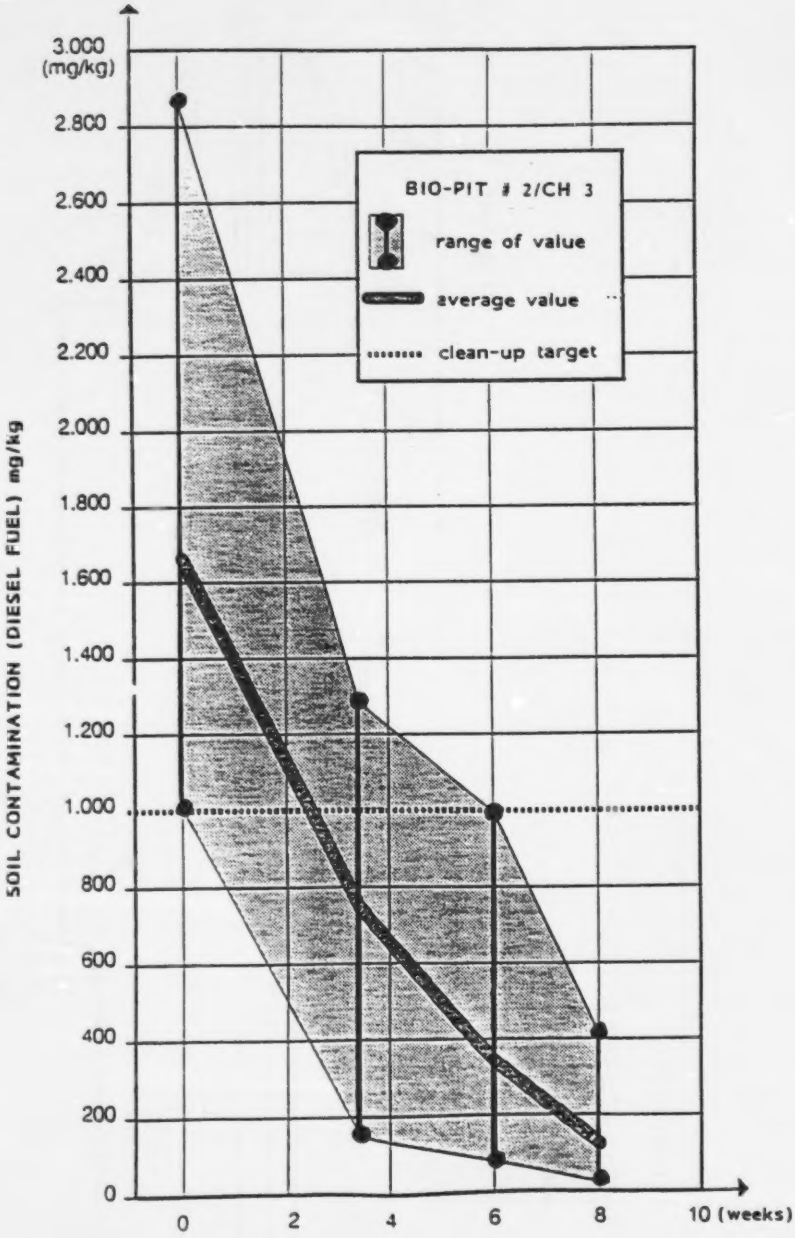
Regarding other pollutants, biodegradation is largely depending on their chemical formula, concentration and agglomaration, the soil character and structure and the presence of toxic or potentially toxic metabolite forming agents.

BIO-PIT PROCESS - SCHEMATIC ILLUSTRATION


bioreactor
circulation tank
irrigation pump
irrigation
HDPE-foil
bio-pit
drainage
sump
pump

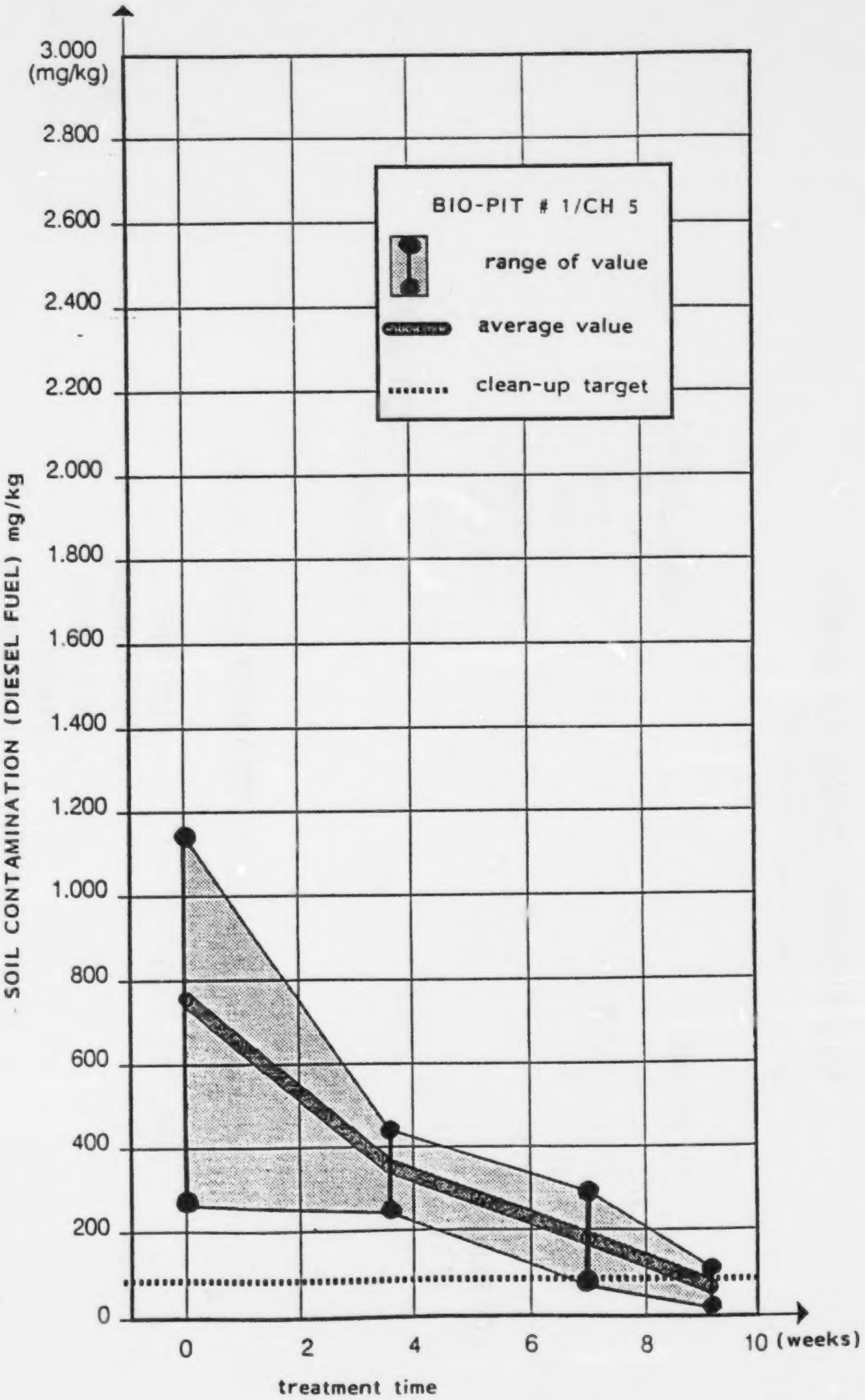
BIODEGRADATION RESULTS

BIO-PIT PROCESS



BIODEGRADATION RESULTS

BIO-PIT PROCESS



BIODEGRADABLE ORGANIC POLLUTANTS
(BIO-PIT PROCESS)

MINERAL OIL PRODUCTS
- GASOLINE
- DIESEL FUEL
- MOTOR OIL
- LUBRICANTS
- KEROSENE
- HEATING OIL

LIGHT AROMATICS
- BENZENE
- TOLUENE
- XYLENE
- STYRENE
- CRESOL
- PHENOLS
- PHENOLIC COMPOUNDS
- XYLENOLES

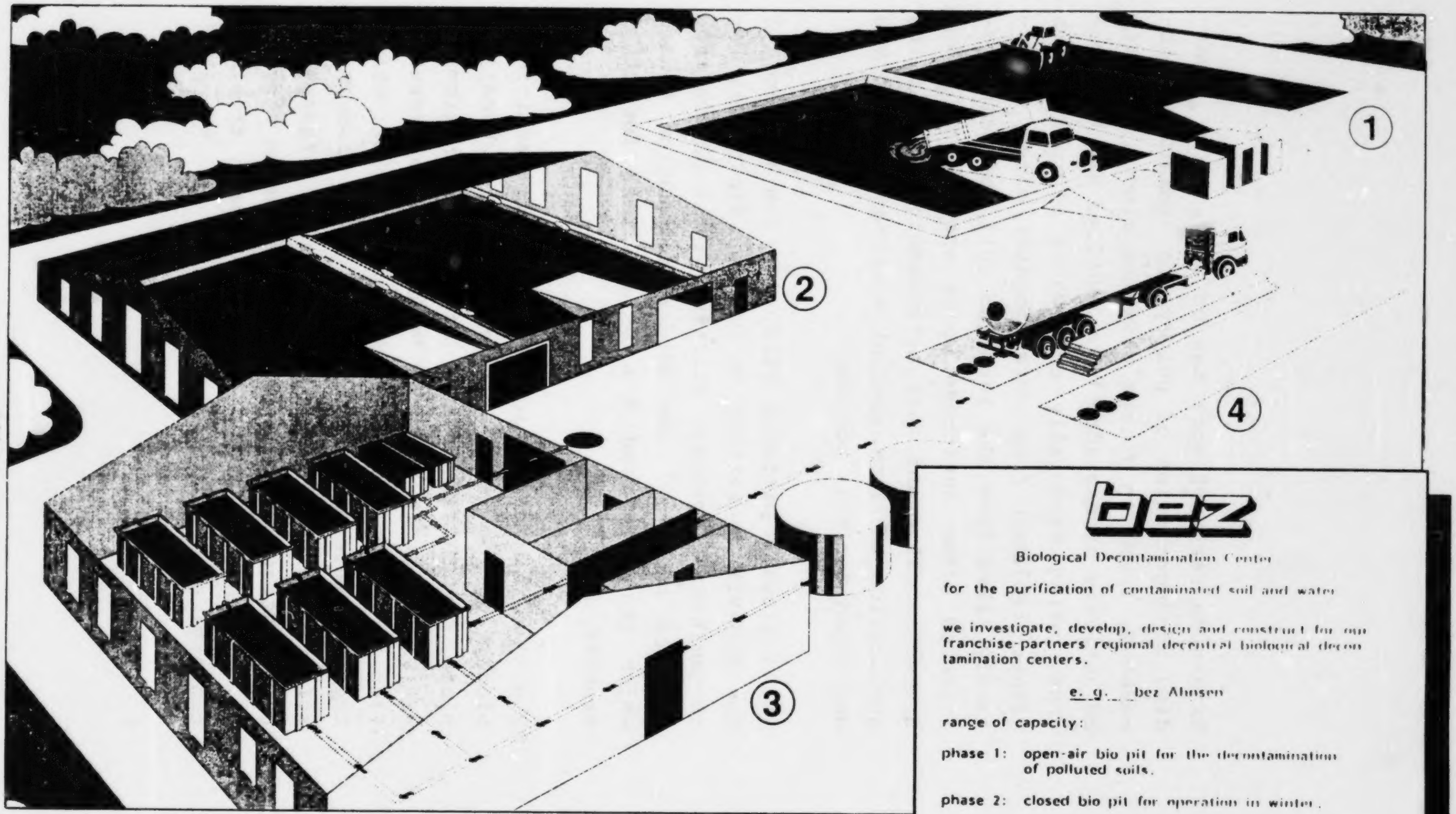
POLYCYCLIC AROMATIC HYDROCARBONS (PAH); e. g.

COAL TAR CONSTITUENTS
- FLUORENE
- PHENATHRENE
- ANTHRACENE
- PYRENE
- FLUORANTHENE
- BENZ(A)ANTHRACENE
- CHRYSENE
- BENZ(A)PYRENE
- BENZ(B)FLUORANTHENE
- BENZ(K)FLUORANTHENE
- DIBENZO(A,H)ANTHRACENE
- INDENO(1,2,3-C,D)PYRENE

Extensive research work has be done, e. g. regarding biodegradation of polycyclic aromatic hydrocarbons, found on former gasworks sites. They can be actively biodegraded by a modified Bio-Pit process, using especially cultivated microorganisms either isolated from corresponding sites or directly taken from the incoming soil and being reinjected after enrichment plus the use of other biomechanical means such as bioemulgators and the application of some special machinery, which was developed for this purpose.

The following pictures will give you an idea of the Bio-Pit operations in various Biological Decontamination Centers, starting with a generalized view of biodetox' own Biodecontamination Center which its pilot and R & D-facilities for other centers.

The then following pictures will show additional biodegradation aids, closing with a schematized plant for the processing of polycyclic aromatic hydrocarbons. It can only be shown as a presentation as it is just presently under construction. These pictures will be followed by a process description showing the treatment of oil-/gasoline- and sandtrap-residues (oil sludges) as an additional moneymaking proposition for these treatment centers.



bez

Biological Decontamination Center

for the purification of contaminated soil and water

we investigate, develop, design and construct for our franchise-partners regional decentral biological decontamination centers.

e. g. bez Ahnsen

range of capacity:

phase 1: open-air bio pit for the decontamination of polluted soils.

phase 2: closed bio pit for operation in winter.

phase 3: bio-reactors for the purification of polluted waters, including industrial waters.

phase 4: washing plant for tank trucks, alternative purification plant for oil sludges.

biodetox®

Gesellschaft zur biologischen Schadstoffentsorgung m.b.H.

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Telefax 0 57 22 / 8 82 82

Coming back to the initial schematized presentation of biodetox' own Decontamination Center you will have noticed that it encompasses a whole package of activities, contaminated soil being just one of them. The speciality of this concept is that it can be expanded in modules, horizontally as well as vertically. A regional decontamination center can be e. g. started with one or more open pits including the specific treatment equipment.

Then a hall can be added, where especially gaseous materials can be handled and the exhaust air can be treated by a biofilter. Then e. g. equipment for the treatment of oil-/gasoline- and sandtrap-residues (oil sludges) can be added. The process was already explained.

The bioreactor farm where polluted waste water can be treated is based on an original idea of our regulatory authorities and can be seen as a third step. Due to the restrictive fines for the uncontrolled delivery of highly polluted industrial waste waters into municipal treatment plants, especially small companies, unable to finance expensive waste water pre-treatment equipment, would have had to be shut down if there had not been an alternative. Therefore the regulatory authorities proposed a bioreactor farm as an appendix to biodetox' biological decontamination center to serve as a pre-cleaning facility for firms within our vicinity including food and vegetable industry, slaughter-houses and others.

This bioreactor farm will be used as well for the treatment of cleaning fluids from a washing station for multi product tank trucks, where detergents, disinfectants and a high quantity of wash water are producing waste water highly loaded with BOD/COD.

Presently, 3 Regional Decontamination Centers are in operation, 2 are under construction and 5 in various stages of planning. The economical operating radius is at roughly 150 miles each. Every one of these centers is strictly based on non-subsidized private regional initiatives, the operators being private companies, usually coming from related fields of activity such as construction, hauling or waste removal. They are cooperating with biodetox on the basis of a general franchise agreement.

The biodetox franchise package contains start-up assistance by a way of expertise, blue prints and all red tape processing regarding the Government and State permits, a complete legal and administrative package regarding waste handling transport and acceptance as well as protection against product liability. Furthermore, biodetox manufactures and ships the equipment and biochemicals to the regional decontamination centers and monitors the biodegradation processes, from time to time improving on the specific formulation and the mechanical process engineering with regard to special pollutants.

At the same time, biodetox runs its own Regional Decontamination Center at the company seat with special facilities for an extensive research and development. R & D is jointly conducted with a number of universities and research institutes. All R & D results are communicated to the franchisees in order to further improve their biodegradation process and reduce the costs involved. This way, biodetox ensures a consistently high quality standard of operating methods nationwide.

The average clean-up charges including an adequate profit- and risk margin for oil contaminated soil, are at 380,00 DM per m^3 or 140 US $/cu-yd., based on a soil kf-factor of 10^{-6} and 3 % equaling 30 000 mg (ppm) diesel fuel per kg of soil before and 500 ppm after a twelve week decontamination process.

The initial investment for the erection of a regional decontamination center as described would be between 500 000 and 1,5 Million US-Dollars with an amortisation rate of ca. three years.

Last not least, you might be interested of what happens to the decontaminated soil after clean-up. Here an agreement with the regulatory authorities has been reached to the extent that soil with a threshold-level of equal or less than 500 mg of mineraloil hydrocarbons per kg of soil can be used for agricultural purposes. Other material with threshold-levels at or above 500 mg up to 1000 mg/kg may be used as cover material for landfills, as road building material or for noise protection walls. Another precondition being that an analysis must prove that there are no soil pollutants at the new site which would add to a further accumulation of pollutants.

Obviously, biological clean-ups, such as conducted in regional decontamination centers cannot be successfully applied to all hazardous wastes. Nevertheless, applying it to all sorts of lower class hazardous wastes as already described precious land fill space and treatment costs can be saved. Furthermore, biological clean-ups are lasting and final. There is no problem transfer into the future or to another place and there are no toxical residues that have to be taken care of.

With regard to these facts the German Federal Government and the governments of various German states are presently giving priority to biological clean-up- and recycling methods. New laws and regulations under way will stress this comittment to assist nature to help itself.

I would now like to summarize and to add that biodetox is interested in licencees worldwide.

Thank you very much for your attention.

Biological remediation of contaminated groundwater and soil – Concepts of remediation and their technical application

M. Kästner [1], **K. Hoppenheidt** [2], **H. H. Hanert** [2]

[1] Department of Biotechnology; Technical University of Hamburg-Harburg, Harburger Schloßstr. 37, D-2100 Hamburg 90, F.R.G.

[2] Institute for Microbiology; Technical University of Braunschweig Biocenter, Konstantin Uhde Str. 5, D-3300 Braunschweig, F.R.G.

Summary:

In this paper different ways to develop biological processes for the remediation of contaminated soil and groundwater are discussed. With dichloromethane as an example it is shown how elimination processes can be developed which are designed for a specific organic pollutant and specific bacteria (Such developments are often to be found in literature). The fixed-bed reactor process presented here is able to achieve results of decomposition of dichloromethane from groundwaters of 4,2 $kg/m^3 \times d$. These results could be maintained for more than six months. As in many contaminated sites bacteria adapted to the organic pollutants are already existing, the example of a contamination with complex organic compounds will be used to show the activation of the microflora from the site to degrade the organic compounds and its technical application in remediation as another way to develop processes. From these investigations a concept of action was developed which permits statements about the possibility of biological remediation of a contaminated site and the processes which can be used, even with relatively few experiments. This concept facilitated the application of biological processes to different organic pollutants in all cases examined until now.

Recent studies show that many microorganisms are not only able to degrade natural organic substrates, but also synthetic organic compounds and components of petroleum. This degradation was mostly to be found under special laboratory conditions, where after suitable times of adaptation the parameter of the respective metabolism were optimally adjusted. Compounds, however, which reached the environment as organic pollutants or hazardous compounds, are persistant in most cases, or are only slightly transformed by the biological activity. If natural compounds were introduced in concentrations not excessively high, on the other hand, they were mineralized by processes of bacterial self-purification, which made use of the whole spectrum of biological types of metabolism. In the course of this the organic compounds may serve as donator and acceptor of electrons, respectively. The different processes of self-purification in soil and groundwaters are represented as biological redox-processes in Figure 1.

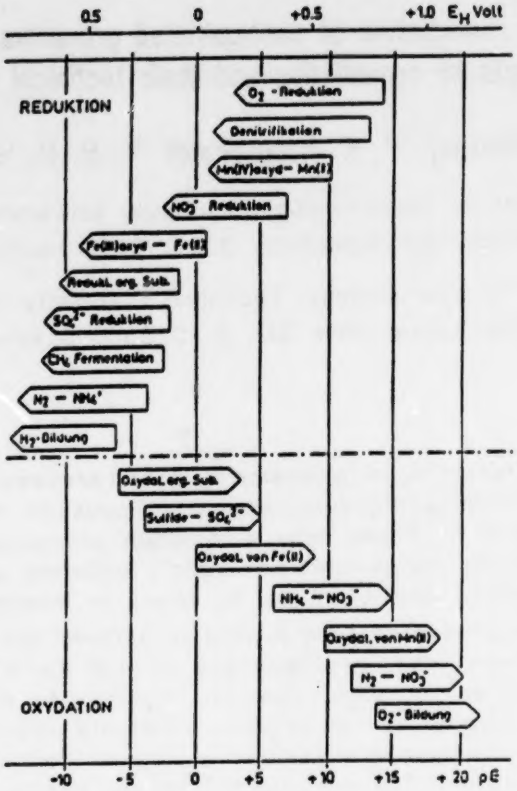

0.5
0
+0.5
+1.0 E_H Volt
REDUKTION
O_2 - Reduktion
Denitrifikation
Mn(IV)oxyd – Mn(II)
NO_3^- Reduktion
Fe(III)oxyd — Fe(II)
Redukt. org. Sub.
SO_4^{2-} Reduktion
CH_4 Fermentation
N_2 — NH_4^+
H_2-Bildung
Oxydat. org. Sub.
Sulfide — SO_4^{2-}
Oxydat. von Fe(II)
NH_4^+ — NO_3^-
Oxydat. von Mn(II)
N_2 — NO_3^-
O_2-Bildung
OXYDATION
-10
-5
0
+5
+10
+15
+20 pE

Fig.1: Biological redox-processes as natural self-purification processes in soil and groundwater (translated from H. Schwoerbel, 1984)

In technical microbiology these microbial self-purification processes are already used to compost organic waste, for sewage treatment, for treatment of waste gas and for the production of drinking water.

Own investigations at different contaminated sites in the Federal Republic of Germany revealed the existence of a microflora which is already adapted to the organic pollutants, but is evidently unable to develop its activity. In many research works described in literature, dealing with the bacterial degradation of specific organic pollutants in the environment, the bacteria were isolated from contaminated sites as well. From that two questions concerning the remediation of contaminated soil and groundwaters follow:

Why don't the self-purification processes work on organic pollutants in the environment, too?

How can remediation-processes be developed from the results of the experiments in laboratory ?

Principally it is to be noted that in contrast to chemico-physical processes microbiological processes can be standardized neither in situ nor on site, as nearly all contaminated sites are to be differentiated because of their different conditions. Technical instructions or standards thus are not yet in sight. However, for the conception of a biological remediation and its necessary microbiological investigations the way of proceeding can be explicity formulated, as will be explained later on.

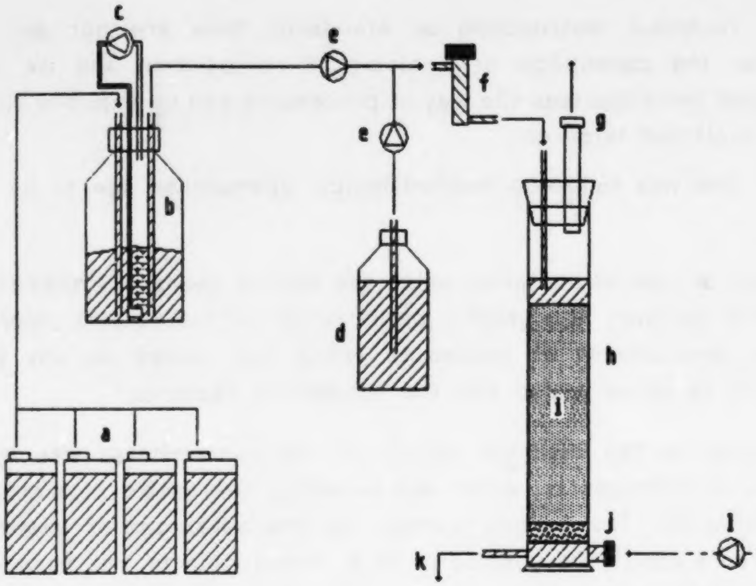
First of all, the two following methodological approaches are to be differentiated:

1). **Isolation of special bacteria, which are able to degrade a specific organic pollutant (possibly the genetic optimization of the strains, too) followed by the development of processes which are suited to the substance which is to be degraded and the respective bacteria.**

2). Stimulation of the microbial activity of the contaminated site by investigations of microcosms, which are suited to the usable physiological type of metabolism. The second method has the advantage of allowing direct statements about the possibility of a remediation of the respective site and the determination of suitable concepts of processes.

The first approach can be explained with the example of dichloromethane degradation. From different contaminated sites caused by dichloromethane pure cultures of Hyphomicrobium species were isolated. These strains are able to grow aerobically with this substance in concentrations up to 1 g/l medium as the sole source of carbon and energy. As these bacteria are known to inhabitate rapid-sand filters used in water supply plants, and these technology is generally used, the idea of using the same technology for the remediation of contaminated groundwaters suggested itself, in order to keep problems of the scale up to full technical scale as small as possible. For the continuous degradation of dichloromethane in a modell groundwater a fixed-bed reactor inoculated by one of the isolated strains was operated. The fixed-bed reactor corresponds to the technology of rapid-sand filters and shall prove the principal suitability of this technology. The process scheme of the reactor is represented in Figure 2.

The degradation power reached by this reactor and the calculated values from that for 1 m^3 plant volume are represented in table 1. The degradation could be kept stable for more than six months. During this time the used strain was not overgrown by other bacteria. Produced biomass was removed by backwashing of the fixed-bed material, at any one time when 100 g of dichloromethane were degraded. The degree of efficiency as well as the concentration of the influent and effluent after a backwashing is shown in figure 3. As these results show that this process can be used in technical applications. Nevertheless for a concrete contaminated site further experiments with the respective groundwater have to be carried out.



a : Stock solution (water, 150 l)
b : Oxigenator
c : Membrane pump (circulation of gas)
d : Stock solution (Mineral salts, DCM)
e : Peristaltic pump
f : Sample port
g : Backwashing drain
h : Fixed-bed reactor (2 l, r = 4 cm)
i : Quartz sand (1.7 l; pore space: 0.28 l)
j : Sample port and backwashing inflow
k : Effluent
l : Backwashing pump

Fig. 2: Process scheme of the fixed-bed reactor for the removal dichloromethane

Table 1: Dichloromethane removal of the fixed-bed reactor

velocity of influent;	detention time*)	influent		effluent		ΔDCM
		DCM	Cl^-	DCM	Cl^-	from ΔCl^-
ml/h ;	min.	mg/l		mg/l		mg/l
2623	6.6	49.2	6.8	n.n	26.6	23.5
5246	3.3	53.7	6.8	n.n	27.3	24.2
10492	1.7	59.0	5.8	2.9	29.8	28.4

vel. of infl.; det. time*)	load DCM	DCM-removal reactor	DCM-removal per m^3 plant vol.
ml/h	mg/h	mg/h	$g/m^3 \times d$
2623	129.0	61.5	869
5246	281.7	126.9	1792
10492	619.0	298.3	4212

*) effective detention time in pore space

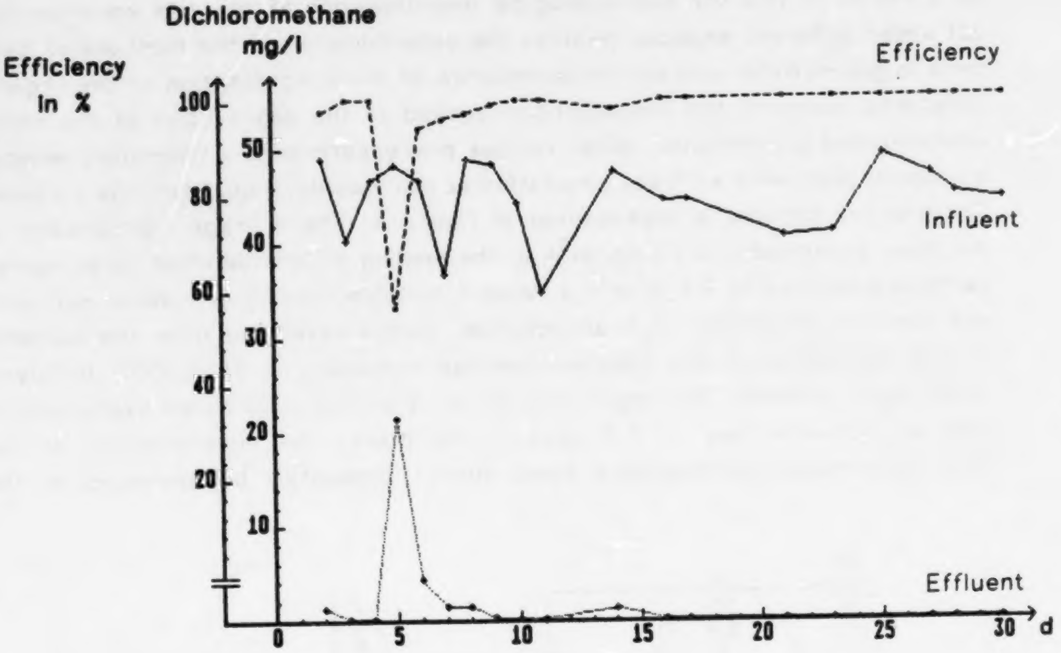
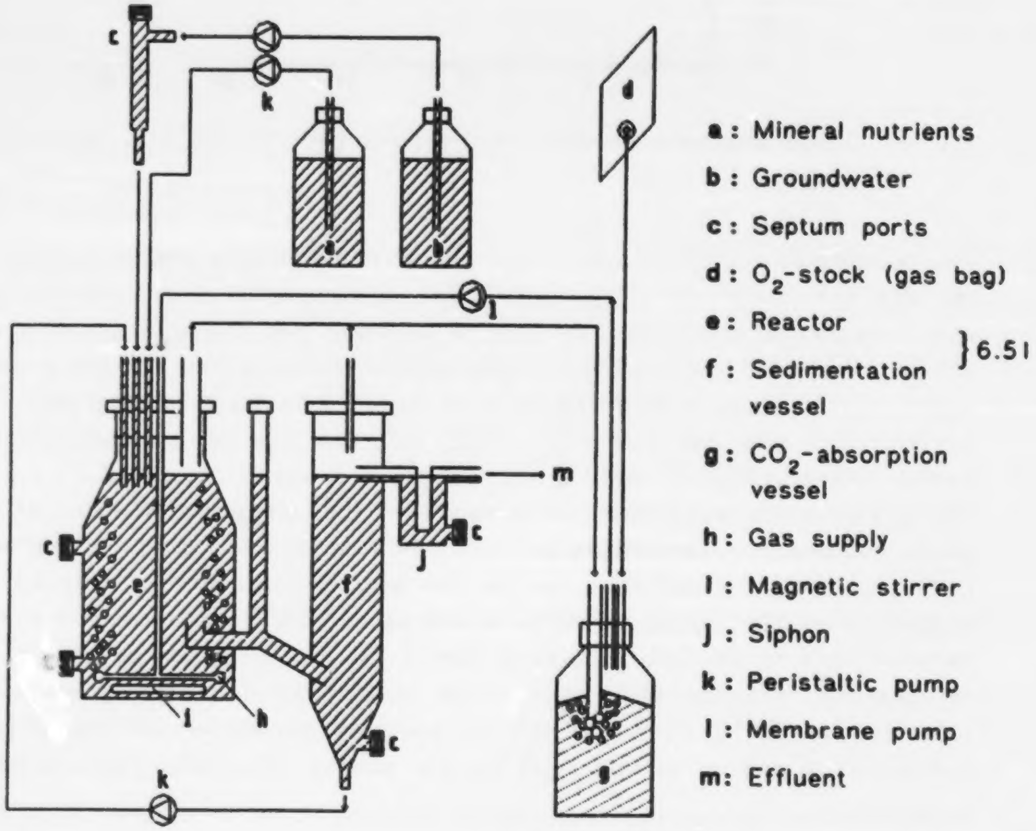


Fig. 3: Dichloromethane removal of the fixed-bed reactor with backwashing (arrow)

The second methodological approach can be exemplified by a special contaminated site in a solvent recycling factory. The contamination of groundwater and soil consisted of a complex mixture of aliphatic and aromatic solvents and volatile chlorinated hydrocarbons. In diethylether-extracts from soil and groundwater over 70 single substances could be detected by gaschromatography. The contaminated area had a size of 10000 m^2, the area of the contamination centre covered 1200 m^2. Until a depth of 25 m (level of groundwater: 4.5 m) the contamination was proved. It is estimated that altogether 40-50 t of aliphatic and aromatic compounds and 4-5 t of volatile chlorinated hydrocarbons had seeped into the soil here. In the soil organic contamination (per kg dry weight) up to 600 mg/kg of aliphatic and up to 700 mg/kg aromatic hydrocarbons were to be found. At some points the concentration of chlorinated hydrocarbons reached 460 mg/kg. The contamination of the groundwater amounted up to 19200 mg COD/l as summary parameter for the organic contamination and up to 150 mg/l for the volatile chlorinated hydrocarbons.

Because of the high contamination and the resulting costs for a chemico-physical remediation it was decided to examine if the site could be remediated biologically. The compound consistence had the consequence that biological remediation processes designed for specific organic pollutants and bacteria could not be used here.

As a result of this the microbiological investigations of the site were carried out under different aspects. Besides the determination of the numbers of bacteria in groundwater and soil in dependance of the concentration of the organic pollutants, parts of the investigations applied to the degradation of the highly contaminated groundwater. After various pre-experiments a laboratory sewage treatment plant with a closed circulation of gas was developed for this purpose. The process scheme is represented in figure 4. The average COD-loading of the plant amounted to 0.73 $kg/m^3 \times d$, the loading of volatile chlorinated hydrocarbons amounted to 3.4 $g/m^3 \times d$. With a suitable feeding of mineral nutrients and electron acceptors (O_2), an activated sludge developed from the bacteria of the contaminated site reached average removals of 95 % COD (influent: 5490 mg/l; effluent: 250 mg/l) and 94-97 % of the chlorinated hydrocarbons with a residence time of 7.5 days in the plant. The mineralization of the toxic chlorinated hydrocarbons could almost completely be assessed by the


c
k
a
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e
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c
c
i
h
c
g
k
a : Mineral nutrients
b : Groundwater
c : Septum ports
d : O₂-stock (gas bag)
e : Reactor
f : Sedimentation vessel
} 6.5 l
g : CO₂-absorption vessel
h : Gas supply
i : Magnetic stirrer
j : Siphon
k : Peristaltic pump
l : Membrane pump
m: Effluent

Fig. 4: Process scheme of laboratory sewage treatment plant

release of chlorine as chloride ions. Concentrations (influent and effluent) of the chlorinated compounds as well as the concentrations of the chloride ions are represented in figure 5. Table 2 summarizes the distribution of specific chlorinated hydrocarbons and release of chloride ions made possible by this.

Batch experiments show that perchloroethylene could only be decomposed in a small amount by the activated sludge; that is why at higher concentrations a side-reaction of this substance has to be made use of. With a shortage of oxygen the sludge dechlorinated tri- and perchloroethylene by way of reduction to cis-1,2-dichloroethylene very fast. By insertion of a unaerated col-

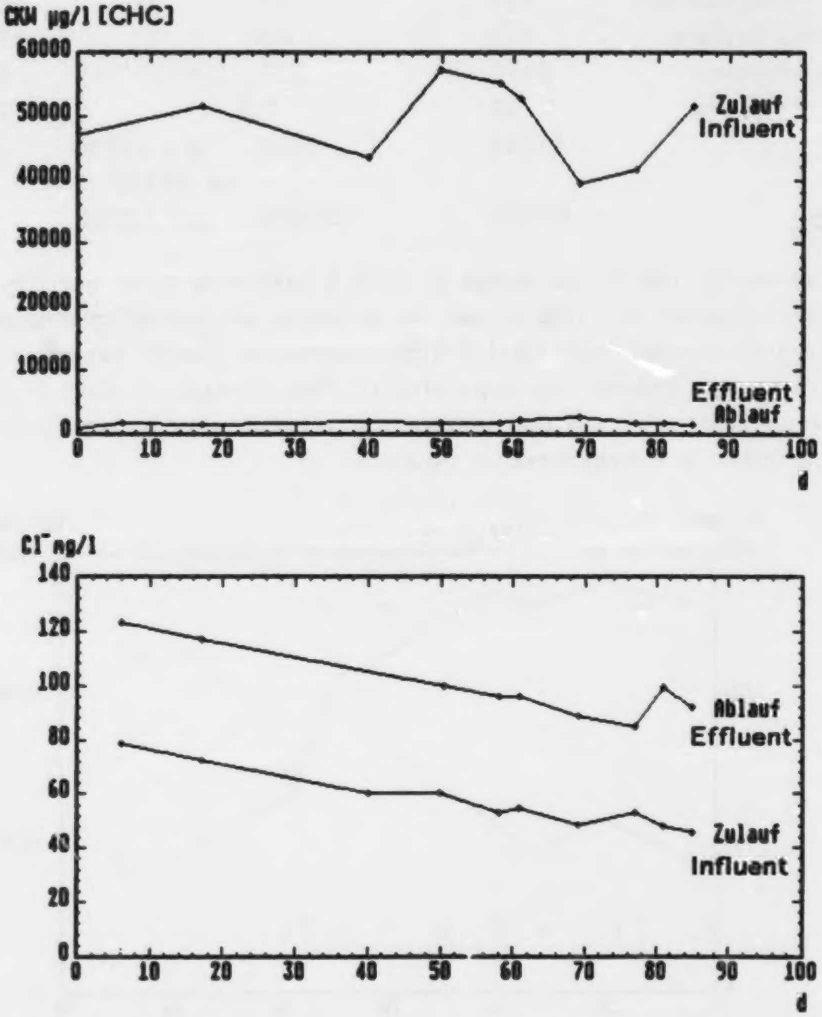

Fig. 5: Influent and effluent concentrations (summarized volatile chlorinated hydrocarbons and chloride ions) from the laboratory sewage treatment plant

Table 2: Distribution of volatile chlorinated hydrocarbons and chloride ions, average concentration of influent and effluent from the laboratory sewage treatment plant

	Effluent µg/l	Influent µg/l		Removal %
Vinylidenechlorid	21.7	0.5		97.6
Dichloromethane	22558	28		99.8
1,1-Dichloroethane	662	183		72.3
cis-1,2-Dichloroethylene	21342	1167		94.5
Chloroform	363	62		82.9
1,1,1-Trichloroethane	153	27		82.3
1,2-Dichloroethane	435	n.n		(99.9)
Trichloroethylene	5471	227		95.9
Perchloroethylene	40	1.2		97.0
Σ CHC	51046	1695	Δ = 49350 (≈ 38800 Cl^-)	96.7
Chloride	57500	100300	Δ = 42800	–

lection vessel for the return sludge (1 l; 16 h residence time) and the feeding of the groundwater into this vessel the available amount of trichloroethylene could be transformed into cis-1,2-dichloroethylene (Batch experiments with perchloroethylene showed the same effect). The increase of cis-1,2-dichloroethylene concentration and the reduction of trichloroethylene concentration in this experiment is represented in figure 6.

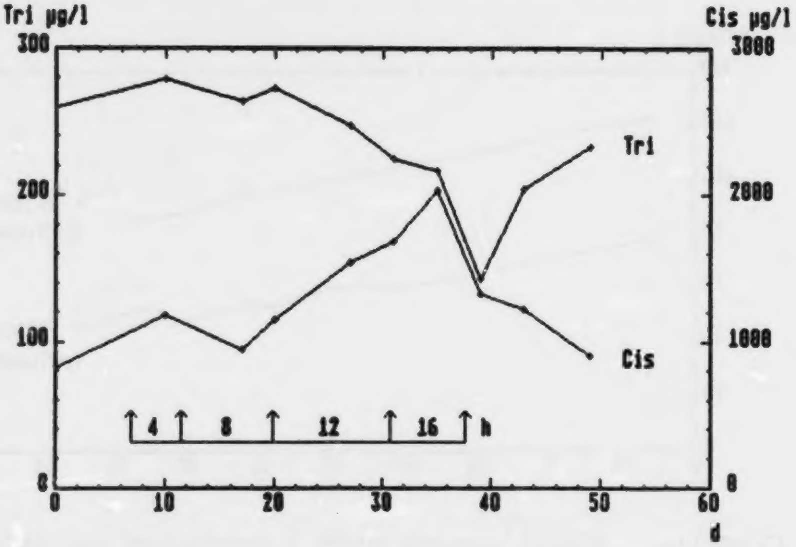

Fig. 6: Effluent concentrations of the laboratory sewage treatment plant at different anaerobic residence times of the backflowing activated sludge

In corresponding experiments with soil columns from the centre of the contamination the degradation of the organic pollutants by the bacteria from the soil could be activated with the addition of minerals (fertilizer) and electron acceptors like O_2 and nitrate. But a detailed degradation balance of the volatile chlorinated hydrocarbons could not be carried out in the soil because of analytical problems.

The results represented here show that in contaminated sites with such a complex composition of pollutants the biological power of self-purification of the soil and groundwater can be activated if conditions are chosen adequately. The persistance of the organic pollutants at this site is due to the limitation of mineral nutrients and electron acceptor supply. It can be derived from the results of the soil experiments that merely the addition of nitrate-containing fertilizers in connection with atmospheric precipitates led to an elimination of the organic pollutants. Thus the soil of the site could be used as an in situ fixed-bed reactor with a remediation time of approx. two years. The seeping of dissolved fertilizer in injektion wells without hydraulic water movement showed the same results for groundwater. The addition of fertilizer was watched with special sampling systems in order to keep the supply of nitrate as an electron acceptor constantly limited against the carbon source. With this secondary contaminations with nitrate could be avoided safely. This process of remediation manages nearly completely without the building of plants above ground and causes only approx. 1/20 of the expense of a chemico-physical remediation. At the moment the remediation in a technical scale is carried out and has led to a 60-70 % reduction of the organic pollutants at the site after just 1.5 years. The details of the remediation will be reported in international journals when the project is concluded.

A summary of the pre-experiments at the site described above also reveals a microbiological concept for the investigations of a site which has to be remediated. This concept will be explained finally. The investigations mainly have to answer the eight following questions, from which the possibility of a biological remediation and the technical process to be applied can be derived.

1). How is the biological state of the contaminated site ?
(quantitative determination of the complete population of bacteria, fungi and actinomycetes; comparison to the situation at the periphery of the contamination; evaluation of the toxic effect of the pollutants upon the microflora)

2). What are the rates of respiration activities of the microflora of the site ?
(physiological evaluation of the self-purification power of the site; respiration of organic carbon sources with and without optimal supply of minerals and electron acceptors)

3). Does a microflora adapted to the organic pollutants exist in the site ? (site specific and pollutant specific evaluation of the self-purification potential under optimal conditions)

4). What are the reasons of the inhibition of the microbial self-purification processes at the site ?
(evaluation of the site specific inhibition potential: toxicity of pollutants, electron acceptor or mineral limitations)

5). How quickly is the biological self-purification carried out with an optimal supply of nutrients ?
(kinetics of the self-purification in batch experiments with discontinuous addition of nutrients; determination of the duration of remedial actions)

6). Which degree of purification can be achieved ?
(the degree of purification should not fall below 90 %, at least under laboratory conditions; determination via summation parameters; for areas with contaminations of chlorinated hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated aromatic hydrocarbons, mineral and tar oils, according to previous experiences corresponding powers of purification are to be achieved even if the contaminations amount to the area of g/kg.)

7). Are organic/anorganic intermediary products with toxic effects on human beeings produced during the purification and how much time does the microflora needs to eliminate these substances, too ?
(e. g. accumulation of vinyl- and vinylidenechloride or nitrite in the metabolism of volatile chlorinatd hydrocarbons)

8). Which technical process should be applied to remove the pollutants on the basis of the experimental results in connection to the situation at the site (extent of pollution; who or what is endangered ?; which use is intended for the site) and under aspects of economy ?

The design of experiments has to be developed in accordance to the specific contaminated site; that means the physiological status quo has to be adapted to the physiology of the degradation of the organic pollutants (see also fig. 1). In this not single the tests of bacteria or substances are concerned primarily, but degradation tests of mixed populations under specific physiological conditions which are possible. The answering of the questions in a phase of laboratory tests of approx. 4 months and the testing of the resulting concepts of remediation in a half-scale technical phase of also approx. 4 to 6 months led to the development of the remediation process for the site desribed above. This concept of action in the meantime also led to the application of biological remediation processes in some cases of contamination caused by mineral oil, tar oil, chlorinated organic compounds originated from the production of pesticides and at sites of former gasworks. The investigations represented here allow to make predictions about the duration and success of a remediation which is to be expected in every specific site. To this a decisive importance is attached by the supervisory authorities in the Federal Republic of Germany. In cases carried out until now the costs of the experiments for each site amounted to 10-20 % of the total remediation costs, depending on the spectrum of pollutants.

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The Holzmann System for In Situ Soil Purification

1. Introduction - Disused Gasworks Sites

During the past decade in West Germany, numerous abandoned or disused gasworks sites and coke plants have been examined with regards to environmental hazards.

By means of the chemical processes involved, and through the coking process of fossile combustibles considerable amounts of tar oils, containing numerous polynuclear(polycyclic) aromatic hydrocarbons (e.g. naphtalene), cyanides, sulphureous substances, and phenol are produced as by-products. In the past, these by-products were separated, stored in basins, and in more or less suitable containers, treated, and then largely used for further chemical or technical purposes.

Through careless usage however, leaking tanks and basins, spillages and in particular as a result of war activities, continuous and high rates of pollution have been discovered at almost every gasworks and coke plant site.

Through the increased environmental awareness of the public including the concern expressed by responsible authorities during the last years, contaminated former gasworks sites have aroused strong public interest.

Most investigations carried out on former sites have revealed serious pollution hazardous for soil, groundwater, and detrimental to human health.

2. Former Gasworks in Bremen-Woltmershausen

During initial soundings in mid-1987 on the site of the former gasworks in Bremen-Woltmershausen, in which between 1900 and 1964 gas had been produced, extremely high contents of tar oil (Polynuclear Aromatic Carbons, PAC) and cyanides were discovered underneath a former tar basin, a gas tank, and a basin for fire-extinguishing water.

Further detailed analyses revealed that below the tar basin about 20000 m³ of medium sand and a layer of clay containing sea silt are contaminated with PAC and cyanides to a maximum depth of approximately 10 m.

Soil specimens were characterised by intensive black coloration and penetrant odor. Analysis of the soil-oil mixture revealed up to 20000 mg PAC/kg and up to 600 mg cyanides/kg.

Fig. 1 shows the characteristic soil profile, grain size distributions, and the qualitative distribution of PAC over depth.

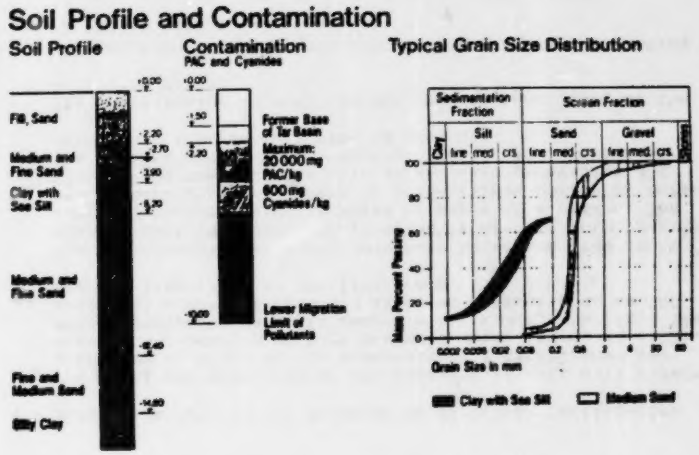


Fig.1: Characteristic soil profile and grain size distribution. Distribution of pollutants.

A layer of silt (clay containing sea silt) approximately one meter thick lies in the quite uniform (U=2) medium sand strata at the center of the contamination. The ground water level lies approximately 2.7 m below the terrain surface.

The highest percentage of PAC was discovered above the silt in the variation range of the groundwater level. The lowest percentage occurs within the silt layer. The sand below the silt layer shows surprisingly high PAC-contamination levels, partly down to considerable depth.

The concentration of the cyanides is distributed less uniformly. A slight cyanide contamination can also be noted in the silt.

Buildings are located directly adjacent to the contaminated area, severely limiting the space available for the soil purification work. Moreover, regular operations on the grounds have to continue during the purification work. Fig. 2 summarises the main characteristics of the contamination.

Main Characteristics of Contamination

Origin	former tar basin of city gas production plant, results of war action
Size	25 x 45 m² and 15 x 32 m² ~ 8 m deep, i.e. ~ 16000 m³ next to existing structures
Contamination	Polycyclic Aromatic Carbons (PAC) Cyanides (CN) in soil and groundwater
Maximum Concentrations	PAC (Σ of 15): 20 000 mg/kg soil (wet) CN (Σ): 600 mg/kg soil (wet)
Soil Properties	- mainly medium to fine, homogeneous sand - layer of clay with sea silt of low permeability

Treatment Methods Considered

Method	Reasons for Rejection
Ex Situ Microbiological Treatment	■ deep excavation next to structure ■ space for composting piles ■ too high concentrations ■ duration
In Situ Microbiological Treatment	■ soil profile and low permeabilities ■ duration
On Site Soil Washing	■ deep excavation required
Thermal Treatment	■ high cost for thermal treatment above 1000 C ■ complex permission requirements
Placement on Hazardous Waste Dump	■ large volumes and high cost ■ deep excavation required
Chosen Method	In situ soil purification by High Pressure Injection (HPI) with mechanical soil-fluid separation and on site water treatment and off site microbiological sludge treatment

Fig. 2: Main characteristics of contamination and treatment methods considered

3. Selection of a Suitable Treatment Method

Disposal of the contaminated soil at a hazardous waste dump was not even considered in detail. On the one hand, a dump suitable for disposal of such large quantities as required was not available. On the other hand, the main objective was to reduce the pollution potential of the contaminated soil to such an extent that the prescribed limits could be maintained and the soil be re-used.

The following methods were examined for suitability:

- Microbiological treatment in situ

  Too high pollutant concentrations in the most contaminated soil portions and a nearly impermeable silt layer excluded this approach as well as the long duration of treatment to be expected.

- Microbiological treatment off site

  Off site processes were also eliminated due to the excessively high space requirements for the composting piles and the expense of transporting the soil. Moreover, unless the soil was prewashed, the high concentration of tar oils would result in intensive adhesion between the soil particles and the pollutants resulting in problems for all microbiological processes.

- Thermic purification

  Temperatures between 1000°C and 1200°C would have been required for purification of the pollutants present. This would have resulted in complete sterilization of the entire quantity of soil. A deep excavation and an appropriate retaining structure would have increased the cost.

- On site or off site soil washing

  The high cost for the required deep excavation and the related groundwater lowering ruled out these methods. Groundwater pumping would have produced tremendous amounts of contaminated water.

Fig. 2 summarises the considered treatment methods and the reasons for their rejection. Because established methods proved unsuitable for the given task of soil purification, a new method of in situ soil purification, developed by the Philipp Holzmann AG, was suggested and laboratory tests carried out to optimise the process parameters. The new in situ soil washing technique, for which several related patents are pending, will be described as follows.

4. The Holzmann System for In Situ Soil Purification

4.1 Basic Principle of the Holzmann In Situ Soil Purification

The first and main step of the Holzmann in situ soil washing procedure is based on the meanwhile well-established construction procedure of high-pressure water injection (HPI). Modern equipment makes it possible to inject water into the soil with a special rotating lance at pressures up to 500 bar and flow rates of 300 liters/min.

For the treatment with high-pressure injection, the contaminated soil requiring purification is divided into individual vertical borings, each jacketed by means of a casing. The actual purification process is accomplished boring by boring, eliminating the need for a large and deep excavation and the related groundwater lowering. The borings overlap in such a way that no soil remains unwashed.

The purification is a multistage process consisting of the following parts:

- separation of pollutants from soil particles and washing of soil in situ
- extraction of soil-water mixture from the ground
- separation of clean particles from water and sludge
- water treatment
- microbiological sludge treatment

- return of purified soil and water into the ground

These steps of the purification process will now be described in detail.

4.2 Stages of the Purification Process

- Placement of Casings

Individual cased borings are used for in situ soil washing to create a clearly defined "reaction volume" for the high-pressure washing, avoiding mutual exchange of pollutants and the need for deep retaining structures.

Hoisted by a rope excavator W 180 an ICE 815 vibrator lowers round steel casings (9.50 m long, 1.50 m in diameter, 14 mm thick) 8.50 m into the ground for a treatment depth of 8.00 m (Fig. 3). The working platform lies 1.2 m below the original ground surface.

The casings are positioned in such a way that they finally form a regular pattern of overlapping borings across the treatment area. The complete soil volume is covered thereby; about 17% are treated twice. Exact measurements ensure verticality of the casings.

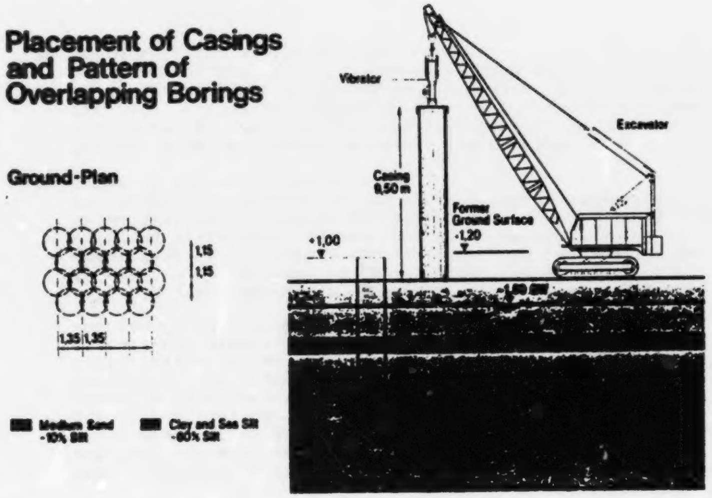

Placement of Casings and Pattern of Overlapping Borings
Ground-Plan
1,15
1,15
1,35
1,35
Medium Sand -10% Silt
Clay and Sea Silt -60% Silt
Vibrator
Excavator
Casing 9,50 m
Former Ground Surface -1,20
+1,00
-1,80 GW

Fig.3: Placement of casings and pattern of overlapping borings.

- High-Pressure washing and Material Extraction

A high-pressure water jet is used to simultaneously separate soil and the tarry, viscous pollutants and supply so much water to the soil that the resulting mixture of soil, water and pollutants can be pumped to the separator unit. Fig. 4 illustrates the process.

A hydraulic excavator (RH 9) suspends an adjustable leader that guides a power rotating head (HDK 800) with a single HPI linkage. While the HPI-lance is lowered at a velocity of 8 cm/min the rotating water jet cuts the soil at a pressure of up to 500 bar and injects 300 liter/min of water into the soil.

Located about 40 cm above the water jet, a strong dredging pump (Toyo ET 10) is lowered simultaneously with the water jet. During high-pressure washing the soil-water-pollutant mixture is pumped above ground.

To avoid seepage of polluted water within the casing towards already purified borings, it is essential to keep the water level within the casing at the same level as the surrounding groundwater. An ultrasonic depth meter, connected to an automatic valve, regulates an additional water supply to the casing to ensure stability of the water level.

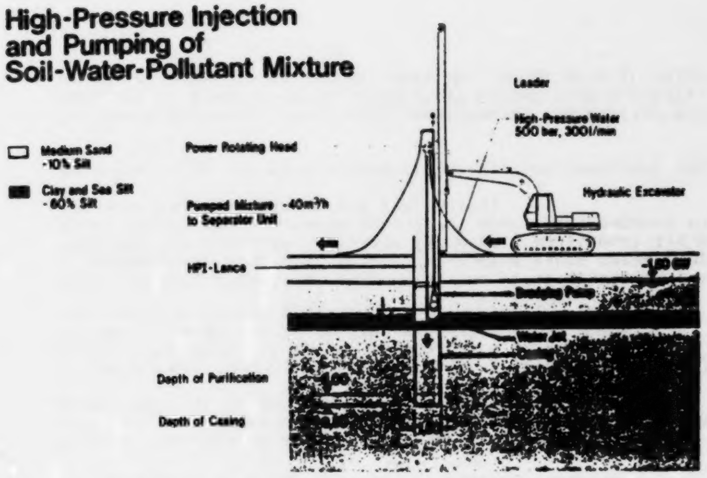

High-Pressure Injection and Pumping of Soil-Water-Pollutant Mixture
Medium Sand -10% Silt
Clay and Sea Silt -60% Silt
Power Rotating Head
Pumped Mixture -40m³/h to Separator Unit
HPI-Lance
Depth of Purification
Depth of Casing
Leader
High-Pressure Water 500 bar, 300l/min
Hydraulic Excavator
-1,80 GW
Dredging Pump
Water Jet
-1,00

Fig.4: Process of high-pressure washing

Separator Unit

Fig. 5 presents a flow chart of the separation process. The contaminated mixture is pumped on to a vibratory sieve, where grain sizes above 3 mm, mainly organic components and little portions of gravel are separated. The passing quantity is pumped into two hydrocyclones in parallel operation with a separation limit at about 60 - 80 µm. Contaminated sludge and water passing the double cyclone are transferred directly to the water treatment plant, designed and run by our joint venture partner Umweltschutz Nord.

At their lower course the hydrocyclones transfer material of grain sizes between 60 µm and 3 mm into an upstream classifier with a separation limit between 100 and 120 µm. Purified grain sizes between 0.1 and 3 mm passing the classifier are dewatered and placed by a conveyor belt ready for return to the open boring after probing and analytical proof of the purification success.

Before, after successful washing, the purified sand (0.1-3 mm) is returned into the open boring, the contaminated water within the casing is carefully exchanged against clean water. Material losses during separation are compensated for by addition of an imported sand rendering similar permeabilities as the original material.

Vibratory pulling of the casings introduces enough energy into the ground to restore the required bearing capacity.

Material between 60 and 120 µm in particle size is passed from the upper course of the upstream classifier on to a drum sieve where it is dewatered.

An additional hydrocyclone takes water passing the dewatering sieve and screens it at 30 µm. The fraction above 30 µm is transfered on to the dewatering sieve where it improves the filter cake.

Fresh water and purified water from the water treatment plant is temporarily stored in a water tank from where three pumps regulate its usage as HPI-water (18 m³/h), additional flushing water within the separator unit (17.7 m³/h), and support water for material extraction from the boring.

An overview of the mass transport through the separator unit gives Fig. 6.

The whole separator unit, newly designed by the Philipp Holzmann AG, is a mobile unit, completely fitted into a single container frame in an upright position, about 10 m in height.

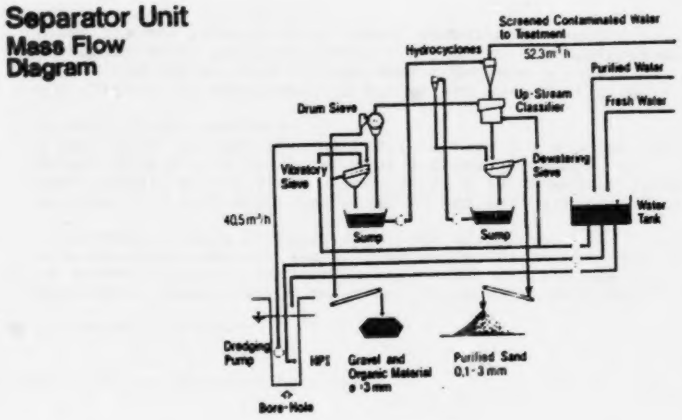

Separator Unit
Mass Flow Diagram
Screened Contaminated Water to Treatment
52,3m³/h
Hydrocyclones
Purified Water
Fresh Water
Drum Sieve
Up-Stream Classifier
Dewatering Sieve
Vibratory Sieve
Water Tank
40,5m³/h
Sump
Sump
Dredging Pump
HPI
Gravel and Organic Material ø >3mm
Purified Sand 0,1-3 mm
Bore-Hole

Fig. 5: Flow diagram of separator unit

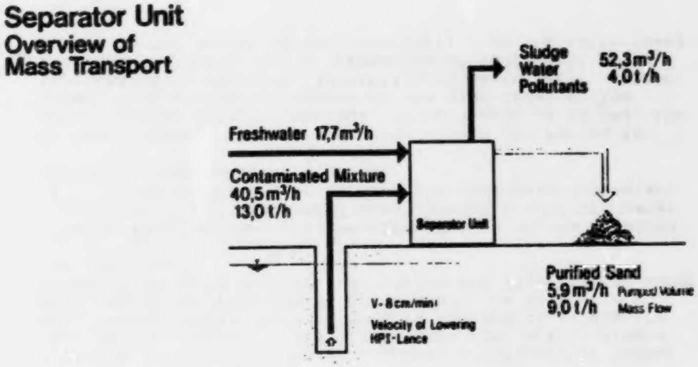

Separator Unit
Overview of Mass Transport
Sludge
Water
Pollutants
52,3m³/h
4,0 t/h
Freshwater 17,7m³/h
Contaminated Mixture
40,5m³/h
13,0 t/h
Separator Unit
Purified Sand
5,9m³/h Pumped Volume
9,0 t/h Mass Flow
V-8cm/min
Velocity of Lowering HPI-Lance

Fig. 6: Mass flow through separator unit

Now the water treatment, that can well be seen as a sequence of standard steps known from sanitary engineering, will be described in brief with emphasis on the special features for the Bremen gasworks job.

- Water Treatment Plant

The sludge-water-pollutant mixture reaching the water treatment plant is first led into flocculation tanks. A screw conveyor transports the flocculated sludge into sieve tanks lined with synthetic mats, where dewatering to a dry substance content of 50% takes place.

In the next stage oily components are skimmed from the sludge-free water using buoyancy effects. A storage tank collects the tar oils.

The oil-free water then passes an activated carbon filter, where polar substances and remaining suspended particles are adsorbed.

The last treatment stage is a cyanide flocculation.

Potable water leaves the water treatment plant into a storage tank from where re-use is directed by pumps. Excess water is returned to the ground via injection wells.

Our partner Umweltschutz Nord has designed and operates the water treatment plant as well as the final sludge treatment to be described next.

- Sludge Treatment

Sludge separated in the water treatment procedure and contaminated by-products of the separation are treated off site microbiologically in composting piles where specially adapted bacteria and substratum are added to optimise the decomposition of the polluted sludge. Within six months the PAC-contents have been reduced by 90 to 98%.

4.3 Overview of the Holzmann In Situ Soil Purification

The described complete cleaning process makes it possible, that no contaminated material has to be deposited as hazardous waste.

For the Bremen gasworks site the described purification process results in a plant arrangement shown in Fig. 7. Fig. 8 summarises the purification and treatment steps and shows their relationships in the whole process.

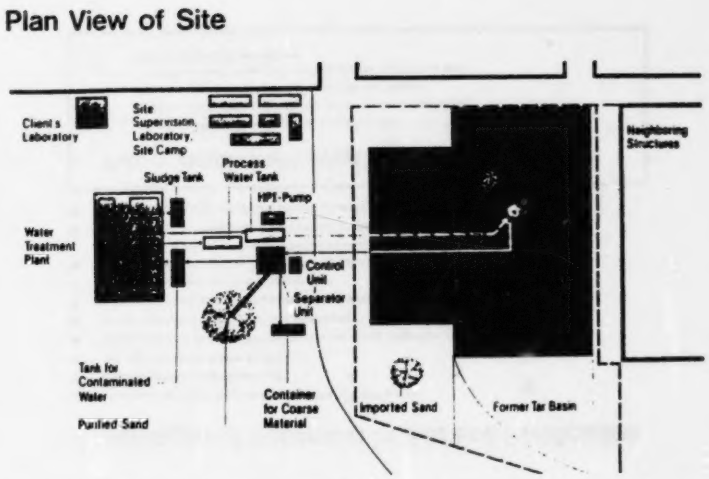

Plan View of Site
Client's Laboratory
Site Supervision, Laboratory, Site Camp
Sludge Tank
Process Water Tank
HPI-Pump
Water Treatment Plant
Control Unit
Separator Unit
Neighboring Structures
Tank for Contaminated Water
Purified Sand
Container for Coarse Material
Imported Sand
Former Tar Basin

Fig.7: Plant arrangement on site

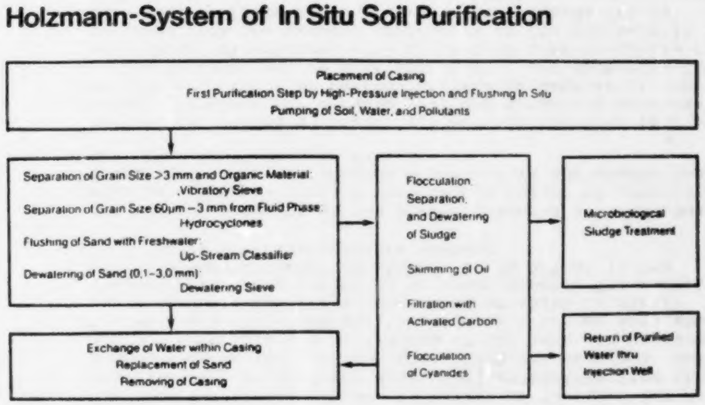

Holzmann-System of In Situ Soil Purification
Placement of Casing
First Purification Step by High-Pressure Injection and Flushing In Situ
Pumping of Soil, Water, and Pollutants
Separation of Grain Size >3 mm and Organic Material: Vibratory Sieve
Separation of Grain Size 60µm – 3 mm from Fluid Phase: Hydrocyclones
Flushing of Sand with Freshwater: Up-Stream Classifier
Dewatering of Sand (0,1–3,0 mm): Dewatering Sieve
Flocculation, Separation, and Dewatering of Sludge
Skimming of Oil
Filtration with Activated Carbon
Flocculation of Cyanides
Microbiological Sludge Treatment
Return of Purified Water thru Injection Well
Exchange of Water within Casing
Replacement of Sand
Removing of Casing

Fig.8:Overview of the Holzmann System of in situ soil purification

5. Purification Results

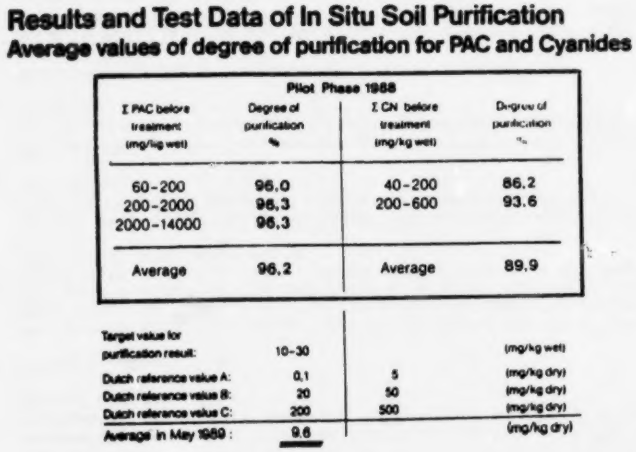
In the pilot phase of the project a detailed field and laboratory testing programme was carried out by an independent supervisor and the Holzmann Environmental Lab.

Individual soil columns (borings) were tested before and after purification treatment.

Typical purification results for optimum action of the pilot treatment plant lay between 98% and 99% reduction of the degree of contamination for PAC. Planned variations of the test boundary conditions and occasional malfunctions reduced the overall average reductions as shown in Fig. 9.

The relative degree of purification is nearly independent of the content of pollutants both for the accumulated content of 16 PAC and a sum value for cyanides.

First results of the main purification contract, under operation since May 1989, are very encouraging. Even for the most critically contaminated soil portions with up to 20000 mg PAC/kg dry soil it is most probable that the guaranteed target value of less than 30 mg PAC/kg will be reached. As average value of the first 30 borings in a heavily contaminated soil portion approximately 5 to 10 mg/kg dry soil were measured after purification.



Results and Test Data of In Situ Soil Purification

Average values of degree of purification for PAC and Cyanides

Pilot Phase 1988

Σ PAC before treatment (mg/kg wet)	Degree of purification %	Σ CN before treatment (mg/kg wet)	Degree of purification %
60-200	96.0	40-200	86.2
200-2000	96.3	200-600	93.6
2000-14000	96.3		
Average	96.2	Average	89.9

Target value for purification result:	10-30		(mg/kg wet)
Dutch reference value A:	0,1	5	(mg/kg dry)
Dutch reference value B:	20	50	(mg/kg dry)
Dutch reference value C:	200	500	(mg/kg dry)
Average in May 1989 :	9.6		(mg/kg dry)

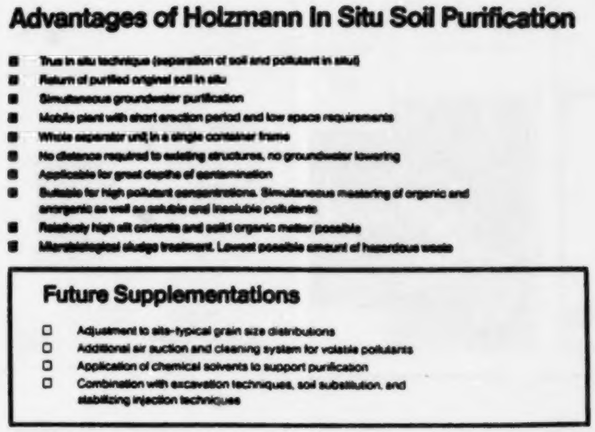
Fig.9: Results of in situ soil purification

6. Summary and Aspects of Application of Holzmann In Situ Purification

The soil purification plant in Bremen is designed for a capacity of 6 m³ soil per hour. Soil extraction from the ground lies on the critical path. With the separator unit about 9 m³/h soil can be treated if the input is continuous. For the extraction and purification of 1 ton of soil about 3.2 m³ process water are used, most of which is partly cleaned water circulating in an inner course. The specific energy demand is about 50 kWh/m³. Up to 80% of it are required by the high-pressure washing.

For the purification of the Bremen gasworks soil the Holzmann in situ purification comprises a number of advantageous properties that were already expressed in the comparison of different approaches in Fig. 2.

However the method also has less obvious features that make it most flexible for a variety of contamination problems and superior to other methods where high degrees of complex contaminations, narrow site conditions, and necessity for restoration of original soil properties come together. Fig. 10 summarises the genuine advantages of the Holzmann In Situ Soil Purification and gives hints towards future supplementations even widening the outlined range of application.



Advantages of Holzmann In Situ Soil Purification

- True in situ technique (separation of soil and pollutant in situ)
- Return of purified original soil in situ
- Simultaneous groundwater purification
- Mobile plant with short erection period and low space requirements
- Whole separator unit in a single container frame
- No distance required to existing structures, no groundwater lowering
- Applicable for great depths of contamination
- Suitable for high pollutant concentrations. Simultaneous mastering of organic and anorganic as well as soluble and insoluble pollutants
- Relatively high silt contents and solid organic matter possible
- Microbiological sludge treatment. Lowest possible amount of hazardous waste

Future Supplementations

☐ Adjustment to site-typical grain size distributions
☐ Additional air suction and cleaning system for volatile pollutants
☐ Application of chemical solvents to support purification
☐ Combination with excavation techniques, soil substitution, and stabilizing injection techniques

Fig.10 Advantages of Holzmann in situ soil purification technique

BIOLOGICAL REGENERATION OF CONTAMINATED SOIL

Volker Schulz-Berendt
Umweltschutz Nord GmbH & Co
West-Germany

1. Introduction

The clean-up of contaminated sites is a matter of topical interest in the area of environmental conservation. Not only as a result of the shut down of industrial plants, such as refineries, service stations and terminals, but also due to accidental spills it is becoming ever more important to find an environmentally- and economically reasonable method for the clean-up of contaminated soil.

The disposal of contaminated soil on dumps can be considered only as temporary solution to the problem.

The biological regeneration is considered to be the better alternative to special waste land disposal for volumes from some hundreds up to several thousand cubicmeters. This process should be preferred in cases where suitable areas in the immediate vicinity of the contaminated site or in its neighbourhood are available and hydraulic clean-up methods cannot be applied for technical reasons e. g. very low permeability of the soil.

Since the biological degradation of organic compounds leads to a valuable product which can fulfill its functions as soil again, this is an ecological valuable method for the clean-up of contaminated sites.

The bioremediation of contaminated soil by microbiological degradation depends on the ability of bacteria and fungi to utilize contaminants as sources of energy and nutrients. It has been well documented that nearly all organic toxins can be broken down to harmless substances by microbes.

Large scale implementation of microbial cleaning techniques has been extremely successful in the treatment of mineral oil spills. Further successes have been observed in the microbial degradation of aromatic and chlorinated hydrocarbons and polycylic hydrocarbons.

2. Approach

The biological degradation-process depends on two requirements:

1. The presence of microbes with appropriate metabolic potentials.
2. Suitable conditions for microbial life and activity in the soil.

On-site and off-site microbial soil regeneration by the TERRAFERM intensified degradation method is designed to realize these assumptions.

Before the beginning of any soil reclamation the ground is analyzed for contaminant contents, nutrient levels and soil structure. Next, the enzymatic turnover potential, the actual microbial activity and the microbial colonization are calculated into a microbiological diagnosis. Based on these results, the most appropriate optimization program for maximal contaminant degradation can be selected and installed. Simultaneously, microbes specially adapted to contaminants are isolated from the soil, carefully examined for suitability, and used as appropriate in the optimization process.

The sorted and classified soil is then subjected to extensive preparatory procedures. Large stones and cement blocks are crushed. Organic substrates are added to improve the soil structure. Mineral nutrients and trace elements are added to support the microbial population. Finally, the soil is cultured with the adapted bacteria and fungi under conditions of intensive oxygenation.

Oxygen is introduced to the system through intensive soil aeration.

In special cases anoxygenic conditions are needed for maximum degradation or oxygen carriers like nitrate or hydrogen-peroxide can be added.

The biological breakdown of toxins takes place in a totally enclosed dynamic fermentation system, in which all parameters, such as temperature, oxygen content, nutrient levels and microbial populations can be maintained at their optimum levels. Volatile pollutants are contained under a specially designed air-discharge biofilter. Leaching water is avoided through careful controls and by preventing rain water from entering the system. Thus, the contaminants do not escape to the environment.

3. Results

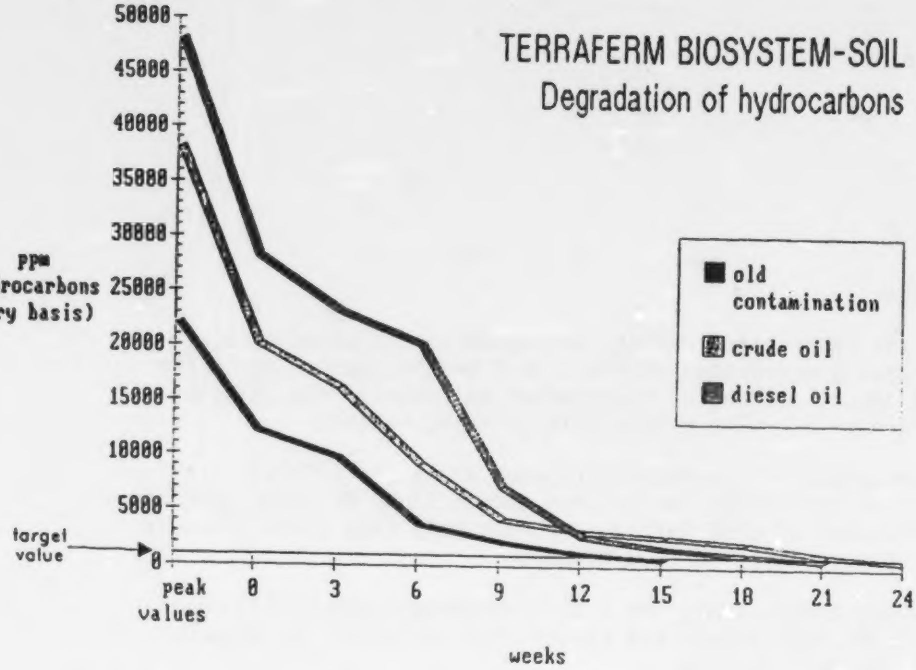
Some of the degradation results are shown in the added charts. Hydrocarbons are degraded within 4 to 8 months, depending on the type and amount of mineral hydrocarbon pollutants. The residual concentrations lie within naturally occuring ranges.

Other contaminants like Polychlorinated Biphenyls (PCB's) need special conditions for optimum degradation. We found that complete breakdown of chlorinated compounds only take place if anoxygenic steps are involved (see graph).

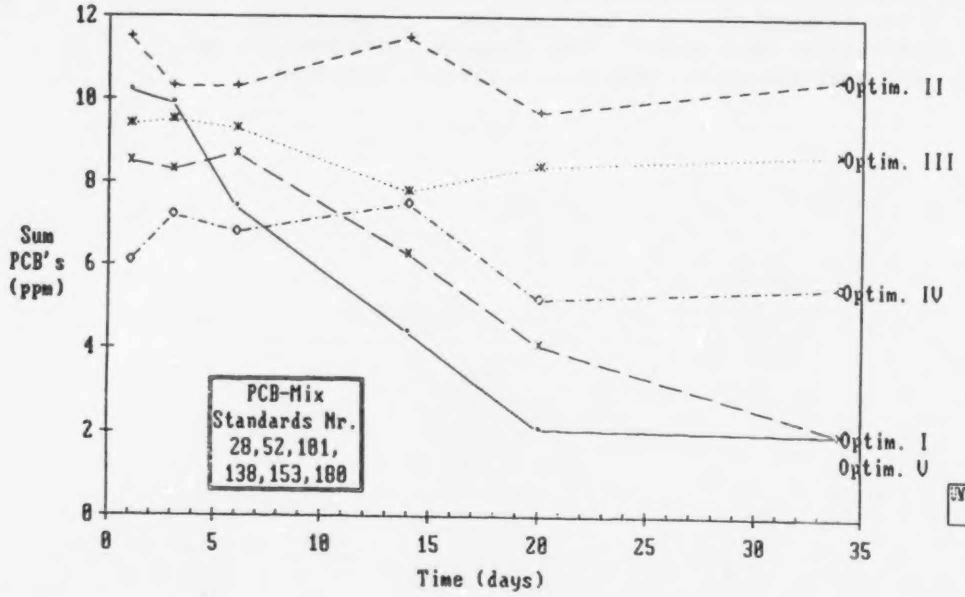
To guarantee these conditions a soil-fermenter with a filling-volume of 200 cubicmeters was constructed to adjust the oxygen-level of the soil exactly.

After regeneration the cleaned soil is testet vigorously chemically and biologically. Aside from measurements of contamination, other characteristics are measured, such as particle size, humus content, water content potential, soil flora and fauna (as well as the ability to support higher plant life), the absence of weeds, and its hygienic suitability for an appropriate future application.

The entire process, from collection of the contaminated soil to delivery of the cleaned soil is under constant biological and chemical supervision. This assures that dangerous residues are not forgotten, and that the prescribed limits are not surpassed.



PCB
Degradation Optimization



UMWELTSCHUTZ NORD GMBH & CO
Fed. Rep. Germany

Ecotechniek

SEVEN YEARS EXPERIENCE IN THERMAL SOIL TREATMENT

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Forum on Innovative Hazardous Waste Treatment Technologies:
Domestic and International

June 1989
Atlanta, Georgia

SEVEN YEARS EXPERIENCE IN THERMAL SOIL TREATMENT

1. INTRODUCTION

Ten years ago, the word soil contamination was not yet known in the Netherlands. There were of course some stories about dump sites in the United States, but that was far away for us. Suddenly, the existence of chemical wastes beneath dwellings was reported. But it was thought to be a single and exceptional case, and with 100 million dollars the whole problem could be disposed of. However, within a short time the number of reported cases of contaminated soil in the Netherlands, had already risen to one case every 6 km^2.

As one of the main companies in Holland in civil constructions and particularly in road construction, Royal Volker Stevin has been endeavouring since 1979 to solve this problem not
only in theory, but also in practice, and, in practice means for us, amongst other things, in such a way that the costs can be justified. For this purpose a special firm with the name Ecotechniek was founded. In 1981 the first plant for soil cleaning was put into operation, and since 1986 a second plant has been providing service. In the near future, several of these plants will be used in Europe.

2. REQUIREMENTS FOR A DECONTAMINATION PLANT

What conditions had to be fullfilled?

- In most cases several contaminating substances are present besides each other. Therefore a cleaning technique must be universal.
- The degree of cleaning must be such that the decontaminated soil can be re-used without restrictions.
- A cleaning operation should not take too much time. An output of 25-50 tonnes an hour is therefore necessary.
- No new problems must be caused. This means therefore that residues are to be avoided.

We needed two years for the development of a process and the construction of an appropriate plant. In the following seven years we gathered a good deal of experience, and realised an enormous number of improvements. During this period decontamination of 600,000 tonnes of contaminated soil has been carried out.

3. PROCES DESCRIPTION

Background and concept of the system can be explained with reference to the schematic drawings of figure 1 and 2. Contaminated soil as a rule has a low organic material content, on avarage about 1 per cent. Therefore contaminated soil cannot be cleaned economically in a normal plant for incineration of chemical waste. A new concept for thermal treatment had to be developed. We opted for a two-phase system. During the first phase (figure 1), the contamination is converted into gases by heating the soil, if necessary up to 550°C.

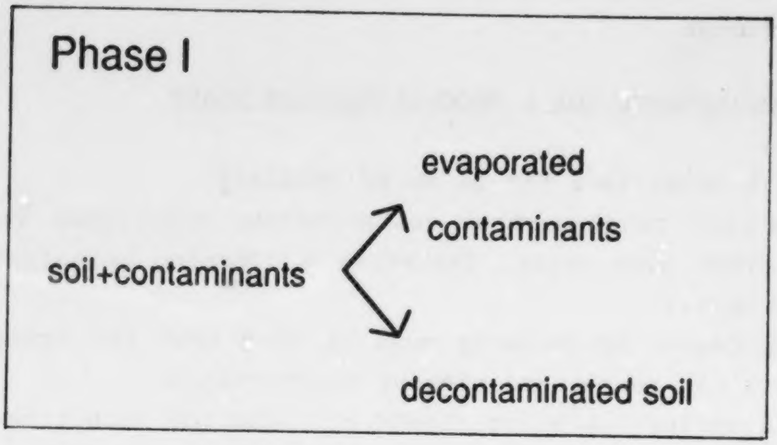

Phase I
evaporated
contaminants
soil+contaminants
decontaminated soil

Figure 1

The developed vapours are separated from the soil, so that the soil left behind, is clean again. This soil is cooled down with water and can then be re-used normally, for example in the site where it came from.

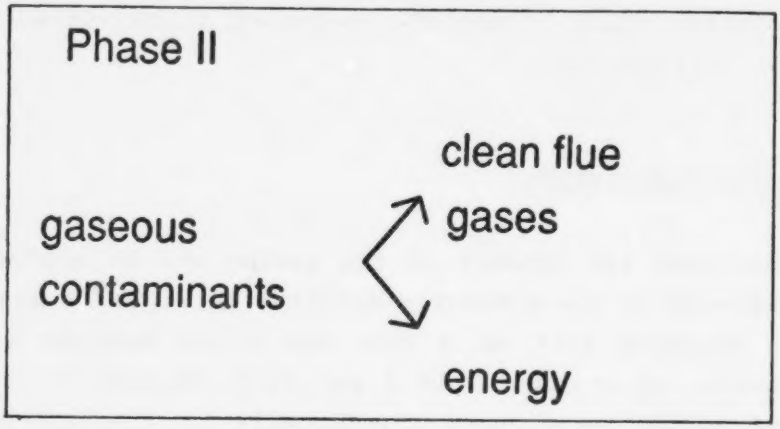

Phase II
clean flue
gases
gaseous
contaminants
energy

Figure 2

During the second phase, the gaseous contamination is destroyed (figure 2). Therefore an afterburning kiln is used. The gases and vapours are burnt with additional oxygen at a temperature of 900°C to 1100°C, or at even higher temperatures if necessary. The destroyed vapours are freed from dust and passed into the stack. In the kiln, of course, a large amount of heat is generated. This heat is utilised for the evaporation of moisture and contaminants in the first phase.

The following scheme therefore arises.

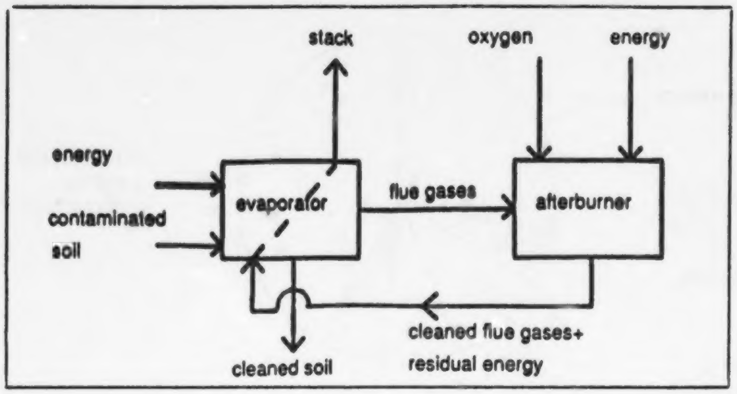

stack
oxygen
energy
energy
contaminated soil
evaporator
flue gases
afterburner
cleaned flue gases+
residual energy
cleaned soil

Figure 3

It will be clear to you that the special technique lies in the evaporator, which is designed like a rotary kiln partly with direct firing and partly with indirect heating by means of the flue gases of the afterburner, and, of course in the combination of the various parts of the total plant.

4. COMPARISON WITH OTHER SYSTEMS

As stated, all poisonous, evaporable organic content of the soil is disposed of, regardless of its chemical structure, quantity and physical state. All types of soil can be processed, although processing is not always equally easy.

The fact that the chemical composition, concentration and type of soil don't need to be taken into consideration distinguishes this process for example in comparison with the biological process. The various washing methods are very sensitive to fine fractions of the soil.
The thermal method, on the other hand, does not eliminate heavy metals and other inorganic substances, although the widespread inorganic cyanide can nevertheless be eliminated very well.

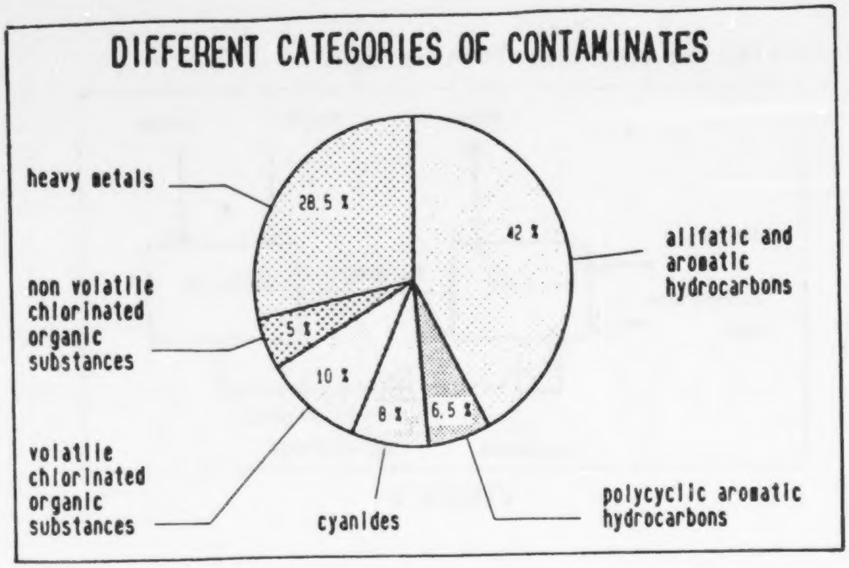


Figure 4

So, a thermal cleaning method does not solve every problem, but the majority of them as you can read from the diagram in figure 4 which describes the distribution of substances in polluted soils in the Netherlands. At least 70 % can be treated thermally. With respect to thermal methods other than the one described in this paper, it must be stated that most of them use a higher, or even much higher, soil temperature. As a result, a lot of energy is consumed unnecessarily, and the normal organic substances peculiar to the soil, such as humic acids, are destructed too.
Hence the soil is not soil any more, but organic free sand which is hardly of interest for re-use purposes.
Due to integrated technology, the plant is very small in relation to its throughput. This allows the construction of semi-mobile machines with a high capacity, an advantage over other systems.

5. CLEANING RESULTS

It is clear that for low-boiling substances, only low evaporation temperatures are required. Table I shows the required temperatures.

In practice, slightly higher temperatures are used. In this table, the required temperatures in the afterburner are listed too.

Table I

required temperature contaminant	evaporation oC	destruction oC
petrol, diesel oil	200-300	750
benzene, toluene, xylene, naphthalene	200-300	800
polycyclic aromatic compounds	450-500	850
cyanides	450	950

Indicative for the cleaning performance of the system are the residual concentrations of PAH's because they are difficult to eliminate and the required residual concentration is low.
As can be seen from figure 5 residual concentrations could be reduced in time due to growing experiences in time.

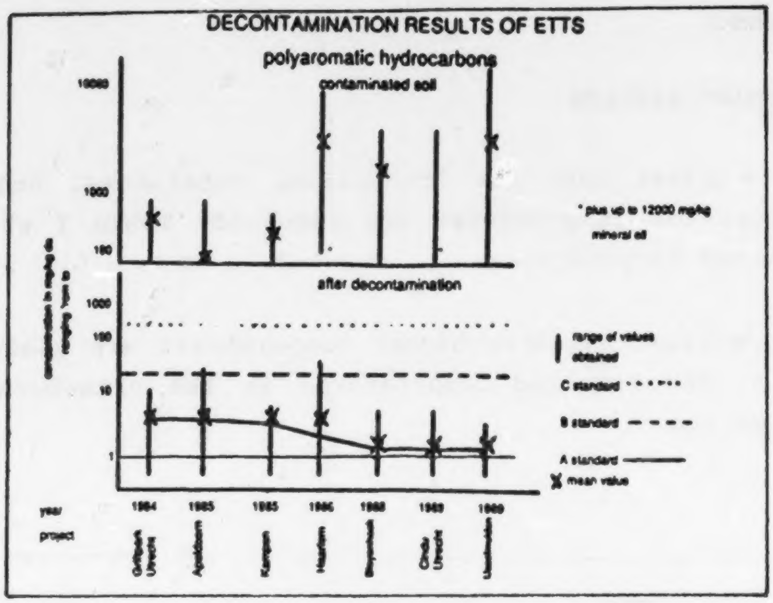


Figure 5

Residual concentrations can be reduced to more or less the level of natural soil (the Dutch A-level), although pollution degrees of processed soils are much higher than at the beginning.

In figure 6 numbers are given for cyanides, a rather often occuring pollutant in the Netherlands, an inorganic and very stable substance as you know.
It seems that the realised resulting concentrations for cyanides have grown through the years, but have a look at the concentrations which are processed.

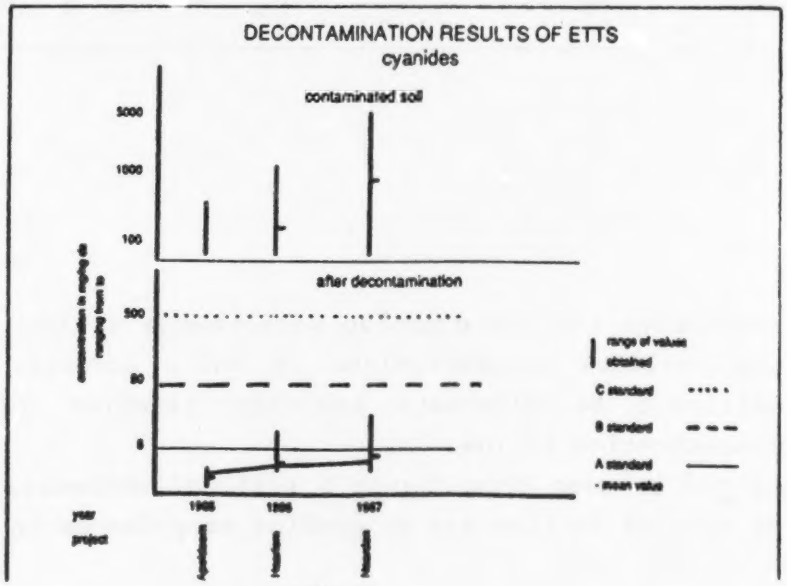


Figure 6

I must point out that the residual concentrations can be reduced as much as you want, but that the price to be payed for that rises more and more rapidly.

PCB's and dioxins have not been mentioned up till now. Contamination with these substances is not widely spread in the Netherlands.
It is therefore only recently that experiments on the decontamination of soils containing these substances have been started. No problems are to be expected with PCB anyway. The boiling points are low, and destruction is fairly easy. The residual concentrations to be obtained are around 1 ppm, and therefore fairly easy. It is just a matter of gathering results of tests and take additional safety measures during execution.

Dioxins have to be reduced to significantly lower residual concentrations and the destruction temperatures are higher, as you know. In four months time, tests will be finished with which it will be proved that dioxin cleaning is possible with this system.

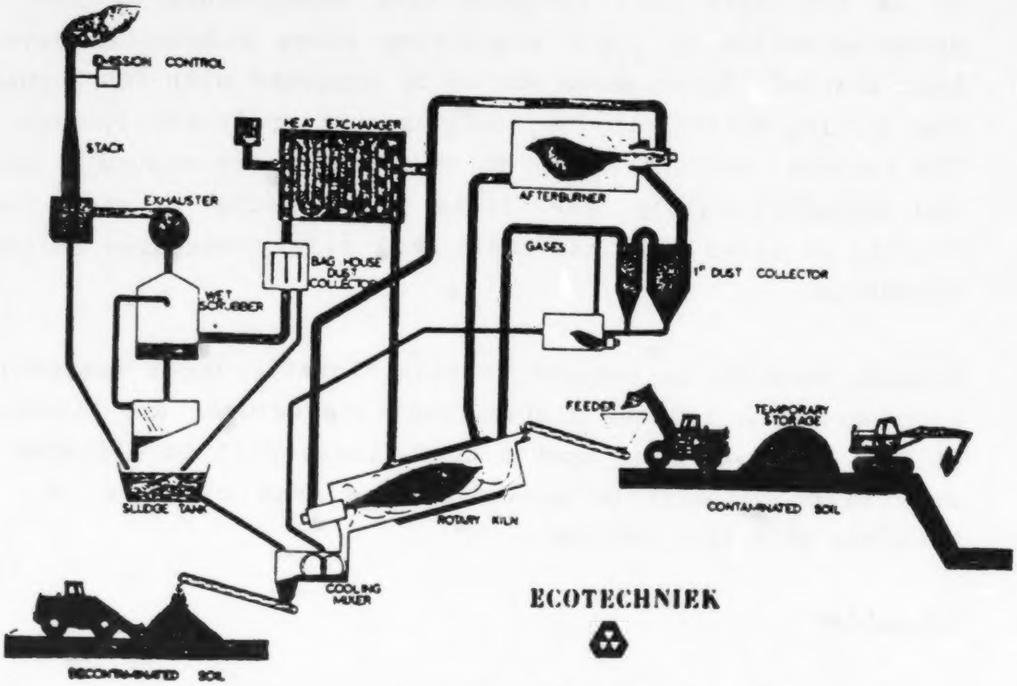
6. EMISSIONS

As already mentioned at the beginning, the process must not lead to any pollution of the environment. The only things which are released are flue gases. These must therefore be freed from dust, SO_2, HCl and HF (if any present).

In particular SO_2 and HCl may be released if sulphur and chlorine containing contaminants are present. Depending on the requirements set with respect to the contaminants to be eliminated and depending on the local regulations on emissions, a flue gas cleaning system is selected.
This means therefore that the plants which are in operation and those which are currently being built all have different flue gas cleaning systems. The concentrations of substances in the gascleaner effluent are that low that the effluent can be used to cool the decontaminated soil. So the system has vertually no residual waste streams.

7. PLANTS

Ecotechniek operates, as stated, two plants, and a third one is under construction that will be in operation in Germany within a few months. The illustration below will give you an impression of the process.


EMISSION CONTROL
STACK
HEAT EXCHANGER
EXHAUSTER
AFTERBURNER
GASES
BAG HOUSE DUST COLLECTOR
WET SCRUBBER
1st DUST COLLECTOR
FEEDER
TEMPORARY STORAGE
SLUDGE TANK
ROTARY KILN
CONTAMINATED SOIL
COOLING MIXER
ECOTECHNIEK
DECONTAMINATED SOIL

THERMAL TREATMENT PLANT E.T.T.S

The soil is sieved and crushed in a preparatory line, to a material size of less than 40 mm. Then it is partially heated indirectly in a rotary kiln. This indirect heating is done with the hot gases of the afterburner. The soil is heated further directly by an oil or gas burner. The cleaned soil is led into a mixer and cooled and moistened with water. The gases from the kiln are passed to an afterburner, in which fresh air and energy are supplied. Special attention is given to energy recovery from the flue gases of the afterburner. The plant has three energy recovery systems, including the rotary kiln.
Furthermore three dust collectors are incorporated, one of which works by a wet process which regulates the pH value of the gases before they leave the stack.

8. COSTS

It is rather difficult to estimate the costs of decontamination of soil with this process in the United States of America.
The costs are not only caused by the process itself but also to a large extend by the moisture content and pollutant content and by safety measurements and environmental regulations.
Moreover we cannot transform our prices simple by exchange rates.
So we can give only a very rough indication. We think that the processing of contaminated soil in the United States with this system will not cost more than $ 200/ton of wet soil.

AN OGDEN COMPANY

OGDEN
ENVIRONMENTAL SERVICES, INC.

CONTAMINATED SOIL REMEDIATION BY CIRCULATING BED COMBUSTION

BY

ROBERT G. WILBOURN
BRENDA M. ANDERSON

This is a preprint of a paper to be presented at the EPA Forum on Innovative Hazardous Waste Treatment Technologies.

MAY 1989

ABSTRACT

The Circulating Bed Combustor (CBC) is an advanced generation of incinerator that utilizes high velocity air to entrain circulating solids in a highly turbulent combustion loop. Because of its high thermal efficiency, the CBC is ideally suited to treat organic wastes with low heat content, including contaminated soil. This paper discusses the development of CBC contaminated soils treatment technology and its application to site remediation. The CBC process, pilot plant, and transportable field equipment units are described. In March of 1989, a Superfund Innovative Technology Evaluation (SITE) demonstration test burn of McColl Superfund site soil was conducted in Ogden Environmental Services' (OES) Circulating Bed Combustion research facility. The results of the successful test are presented herein. The paper also reviews the on-going site remediation activities in Alaska and California using OES designed, fabricated and deployed transportable CBC units.

CBC PROCESS DESCRIPTION

The CBC is ideally suited to treat feeds with low heat content, including contaminated soil. Figure 1 shows the major components of a CBC configured for soil treatment. Soil is introduced into the combustor loop at the loop seal where it immediately contacts hot recirculating soil from the hot cyclone. Hazardous materials adhering to the introduced feed soil are rapidly heated and continue to be exposed to high temperatures throughout their residence time in the ceramic lined combustor loop. High velocity air (14 to 20 ft/s) entrains the feed with circulating soil which travels upward through the combustor into the cyclone. Retention times in the combustor range from 2 seconds for gases to ~30 minutes for larger feed materials (<1.0 in.). The cyclone separates the combustion gases from the hot solids, which return to the combustion chamber through a proprietary, non-mechanical seal. Hot flue gases and fly ash that are separated at the cyclone pass through a convective gas cooler and on to a baghouse filter which removes the fly ash. Filtered flue gas then exhausts to the atmosphere. Heavier particles of purified soil remaining in the lower bed of the combustor are removed at a controlled rate by an ash conveyor system. As a consequence of the high turbulence in the combustion zone, temperatures around the loop (combustion chamber, hot cyclone, return leg) are uniform to within ±50°F over the typical operating range of 1450 to 1800°F. The uniform low temperatures and high solids turbulence also help avoid the ash slagging that is generally encountered in other types of incinerators.

Acid gases formed during destruction reactions are rapidly captured in the combustor loop by limestone that is added directly into the combustor with the feed. HCl and SO_2 that are formed during the combustion of chlorine and sulfur bearing wastes react with limestone to form dry calcium chloride and calcium sulfate, (benign salts). Due to the high combustion efficiency attainable in a CBC, an afterburner is not needed. In more than 90% of the cases studied to date, post-combustor acid gas scrubbing is not required. Emissions of CO and NO_x are controlled to low levels by the excellent mixing resulting from the turbulence, by the relatively low temperatures and by staged combustion that is achieved by injecting secondary air at locations ascending the combustor.

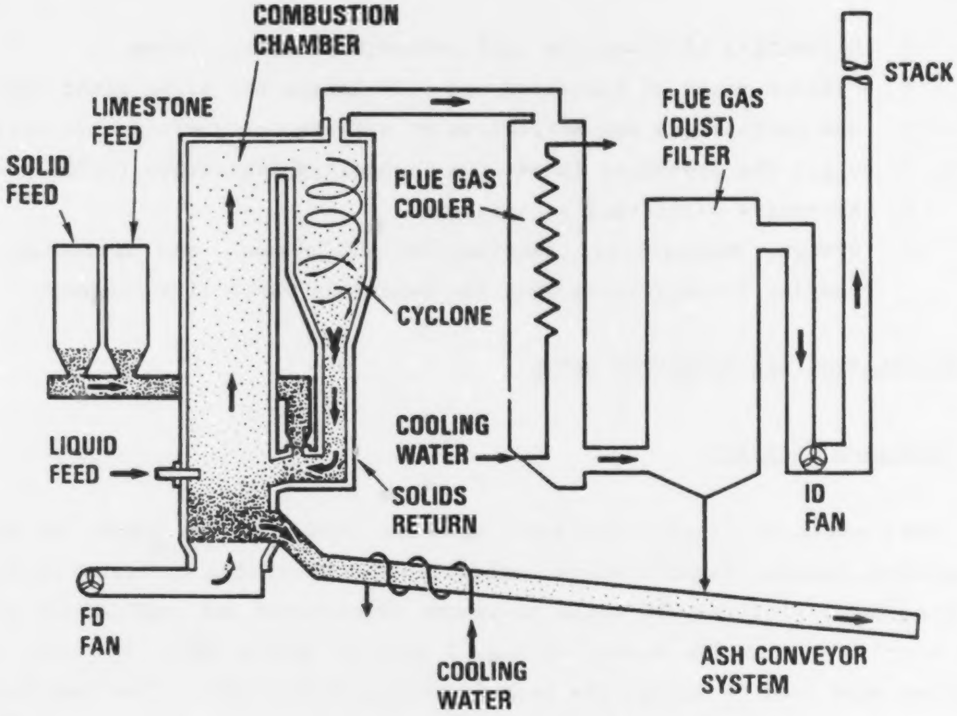

COMBUSTION CHAMBER
LIMESTONE FEED
SOLID FEED
LIQUID FEED
FD FAN
FLUE GAS COOLER
CYCLONE
COOLING WATER
SOLIDS RETURN
COOLING WATER
FLUE GAS (DUST) FILTER
STACK
ID FAN
ASH CONVEYOR SYSTEM

Fig. 1. Schematic Flow Diagram of Circulating Bed Combustor for Soil Treatment

Because of these design and operating features, the CBC can attain required DREs for both hazardous wastes (DRE 99.99%) and toxic wastes (DRE 99.9999%) at temperatures below those used in conventional incinerators which typically burn at temperatures greater than 2000°F.

The Circulating Bed Combustion technology is well developed and is being applied on two contaminated soil site remediation projects that will clean over 80,000 tons of contaminated soils. Ogden Environmental Services, Inc. (OES) and its predecessors have pursued a systematic technology development and an applications approach comprised of the following elements:

- Definition of treatable soil contaminant wastes types
- Fifteen years of fluidized and circulating bed pilot plant testing
- CBC performance demonstrations in private and governmental programs, e.g., the Superfund Innovative Technology Evaluation (SITE) program
- Extensive permitting activities
- Design, engineering, fabrication, deployment, and operation of modular transportable CBCs for hazardous waste site cleanups

OES CIRCULATING BED COMBUSTOR UNITS

Research Facility

OES' research Circulating Bed Combustor (CBC) is the heart of an integrated, highly flexible waste combustion demonstration facility located in San Diego, CA. Initial CBC-soils treatment development and engineering studies were carried out in the 16-in. (i.d.), 2 million Btu/hr CBC. The test data obtained were used to design the larger, transportable CBCs. The configuration of the research CBC is shown schematically in Figure 1. Figure 2 is a photograph of the 16-in. CBC unit. The 16-in. CBC design features and capabilities are summarized in Table 1.

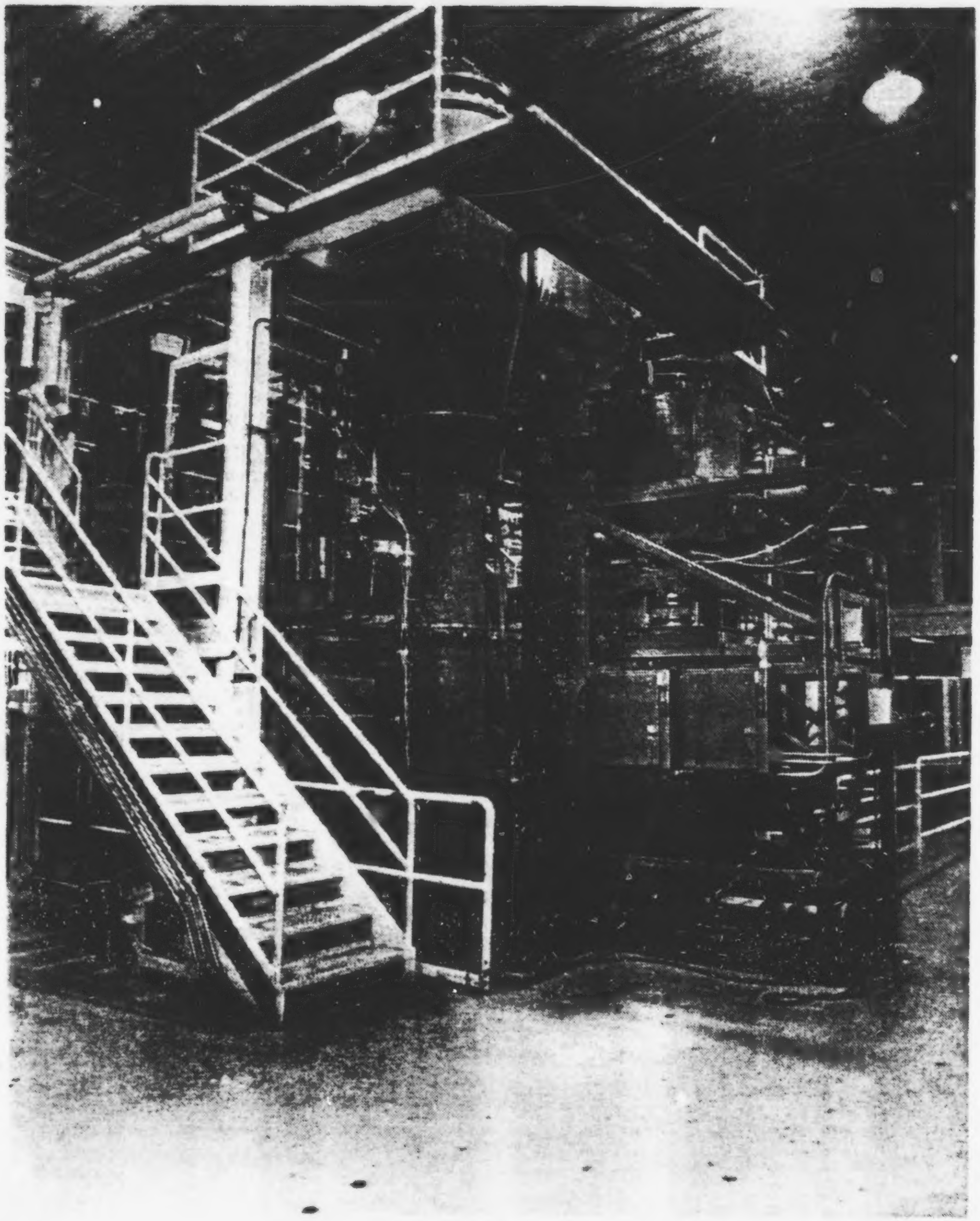


Fig. 2. 16-in. CBC in the San Diego Research Facility

TABLE 1

16" - DIAMETER CBC DESIGN FEATURES AND EQUIPMENT CAPACITIES

Combustor size	
Inside diameter, in.	16
Height, ft	27
Normal operating temperature, °F	1400 to 1800
Maximum outside surface temperature, °F	200
Auxiliary fuel maximum thermal output, MMBtu/h	2
Soil feeder maximum throughput, lb/h	2000
Sorbent feeder maximum throughput, lb/h	200
Bed ash removal system maximum throughput, lb/h	2500
Liquid feeder maximum throughput, gpm	30
Continuous on-line flue gas analysis	0 to 25% oxygen 0 to 25% carbon dioxide 0 to 1000 ppm carbon monoxide 0 to 1000 ppm nitrogen oxides 0 to 1000 ppm unburned hydrocarbons 0 to 1000 ppm sulfur dioxide
Baghouse filters	
Total surface area, ft^2	550
Number of filters	50
Flow capacity, acfm	800
Maximum operating temperature, °F	375
Forced-draft fan	
Maximum pressure, psig	12
Maximum flow, scfm	500
Induced-draft fan	
Maximum vacuum, in. w.g.	50 (at 800 acfm)

Transportable CBC's

The transportable 36-in. (i.d.), 10 million Btu/hr CBC consists of seven structural steel modules that contain the process equipment and provide the structural framework of the CBC. The modules do not exceed measurements of 8 feet 6 inches wide, 10 feet 4 inches high, and 35 feet long. As a result, the modules can all be transported on single drop trailers that do not require special highway transportation permits. The CBC cyclone and combustor are mounted to the top of one of the structural modules. When erected, the transportable CBC itself sits on a pad of 30 by 50 feet and is approximately 60 feet in height. In field operations, the transportable CBC's are incorporated in a complete system layout which includes ancillary equipment units and transportable buildings, e.g., a control room, a motor control center, an analyzer room and a chemistry support laboratory (optional). Figure 3 is a schematic drawing of the transportable CBC. Figure 4 is a photograph of a field assembled transportable 36-in. (i.d.) CBC unit.

CBC RATE THROUGHPUTS

CBCs have been constructed and operated with thermal ratings that range from 2 million Btu/hr to 50 million Btu/hr. The soil throughput of these units varies in response to the moisture content of the feed and to its energetic value. Figure 5 compares the relative throughputs of several CBC sizes for various feed streams.

MEDIA TREATED

Circulating Bed Combustion is widely applicable to many hazardous waste forms. Solids, e.g., contaminated soils, liquids and sludges are treated with equal facility by using the appropriate feeding systems. OES has conducted extensive pilot plant and field unit testing on soils contaminated with hydrocarbons and chlorinated hydrocarbons.

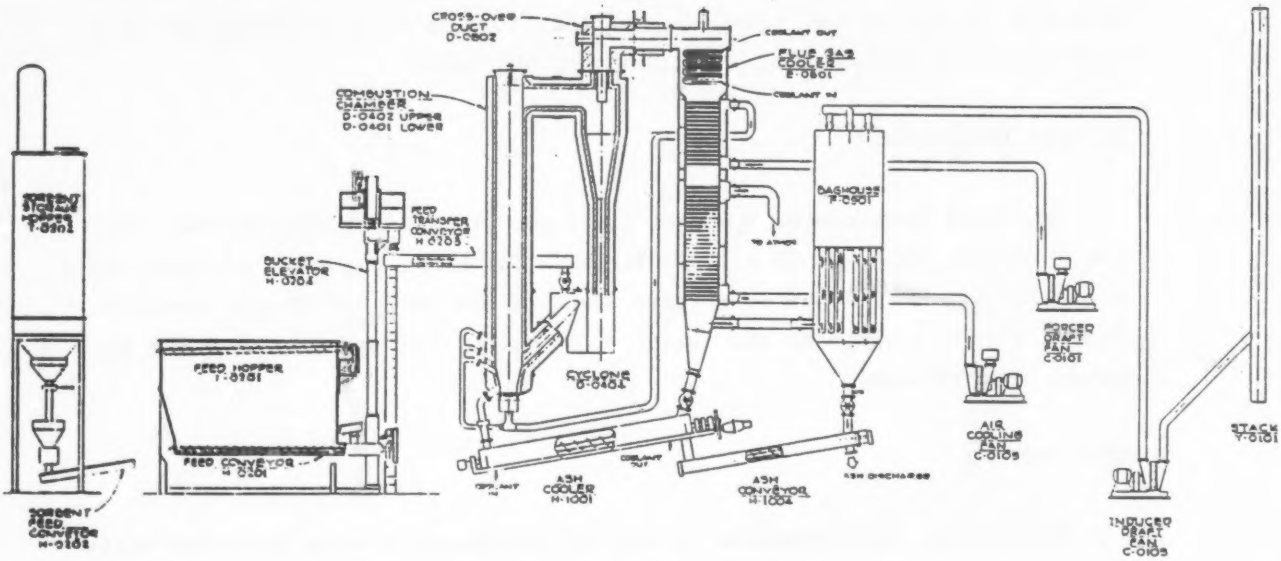

CROSS-OVER DUCT D-0802
COOLANT OUT
FLUE GAS COOLER E-0801
COOLANT IN
COMBUSTION CHAMBER D-0402 UPPER D-0401 LOWER
SORBENT STORAGE HOPPER T-0202
FEED TRANSFER CONVEYOR H-0203
BUCKET ELEVATOR H-0204
TO ATMOS
BAGHOUSE F-0801
FORCED DRAFT FAN C-0101
FEED HOPPER T-0201
CYCLONE D-0401
AIR COOLING FAN C-0105
STACK Y-0101
FEED CONVEYOR H-0201
COOLANT IN
COOLANT OUT
ASH COOLER H-1001
ASH CONVEYOR H-1004
ASH DISCHARGE
SORBENT FEED CONVEYOR H-0202
INDUCED DRAFT FAN C-0103

Fig. 3. 36" Diameter Transportable CBC Schematic

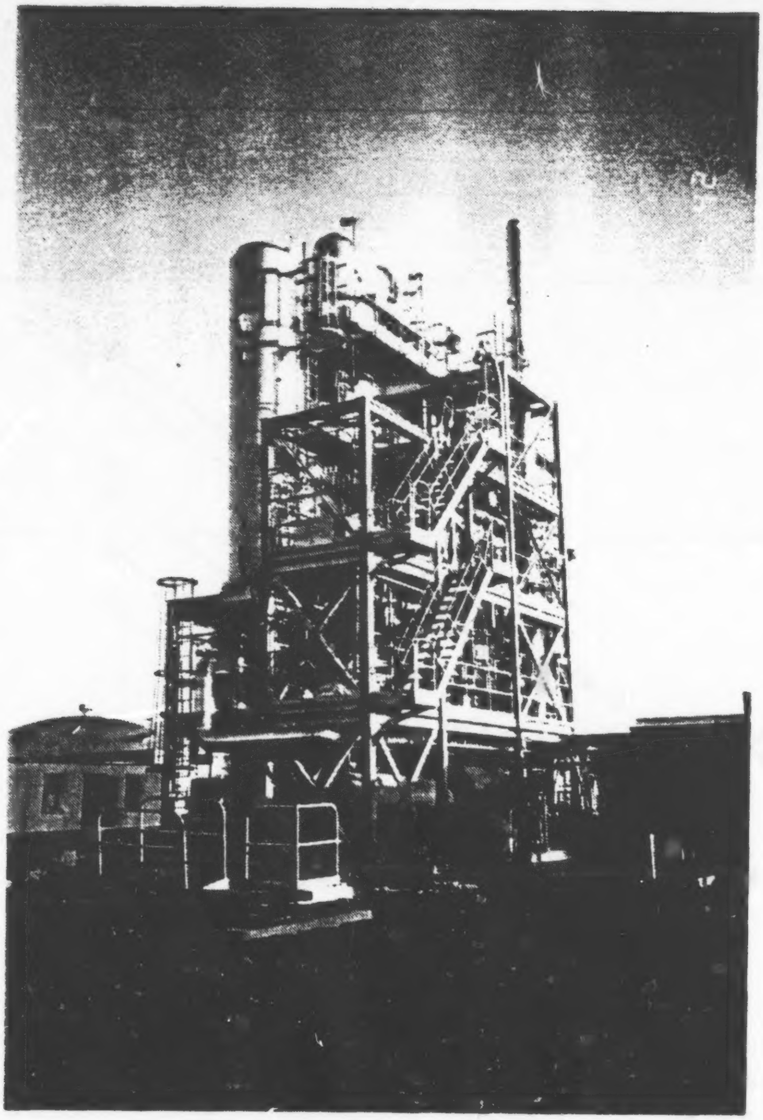


Fig. 4. Field Assembled Transportable CBC Unit

LEGEND	WASTE DESCRIPTION	WATER CONTENT %	HEAT CONTENT Btu/LB	THROUGHPUT (LB/HR) VS. COMBUSTER ID.					
				16 IN.	24 IN.	36 IN.	48 IN.	60 IN.	104 IN.
■	PCB CONTAMINATED SOIL	10	0	1,260	2,840	6,380	11,340	17,720	53,240
□	PCB CONTAMINATED SOIL	20	0	930	2,080	4,680	8,320	13,010	39,130
●	CHLORINATED CHEM. SLUDGE	80	1,331	440	1,000	2,250	4,000	6,250	18,770
○	CHLORINATED CHEM. SLUDGE	40	4,000	340	770	1,740	3,100	4,840	14,530
▲	CHLORINATED LIQUID WASTE	4	7,606	210	470	1,060	1,880	2,940	8,840
△	OIL AND SOLVENT WASTE	13	11,227	130	280	740	1,140	1,780	5,340

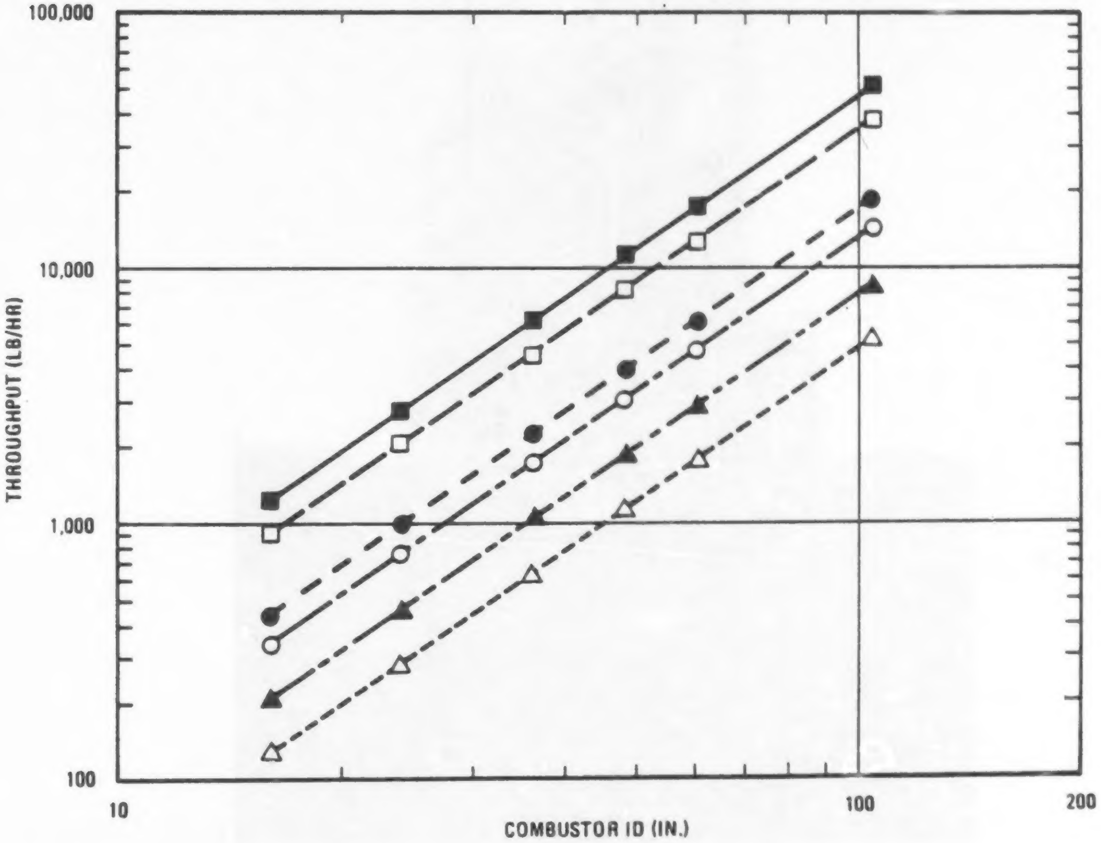


Fig. 5. CBC Unit Size Throughput Comparisons

PROCESS WASTE STREAMS

The CBC process typically produces solids (i.e., bed and fly ash) and stack gas, as shown in Figure 1. The composition of the stack-gas system effluent must meet stringent EPA and other governmental requirements in accordance with permitted conditions. All the CBC incineration tests of contaminated soils verify that the purified soil treated by the CBC is non-hazardous with respect to organic residuals. Since most metals report to the ash during combustion, the disposition of ash is specific to each waste feed case and must be determined on an individual basis. For most organic-contaminated soil sites, the ash produced by the CBC meets the criteria for redeposition on site. Post-combustion fixation processes may occasionally be required if the ash metals content or leachability exceeds permissible levels.

RECENT OES TEST PROGRAMS WITH CONTAMINATED SOIL FEEDS

Superfund Innovative Technology Evaluation (SITE) Program

In 1986 OES's CBC technology was selected by EPA for a demonstration under the SITE program. Contaminated soil from the McColl Superfund site in Fullerton, California was selected as the waste feed for the demonstration. Due to multiple delays encountered in the securing all of the required permits, it was not possible to conduct the planned feasibility demonstration test until this year.

The treatability study was conducted during the week of March 27, 1989 in the combustion demonstration facility. The study covered approximately 31 hours during a four-day period. The study was monitored by EPA, the California Department of Health Services, and the San Diego County Air Pollution Control District. A test profile is given in Figure 6. A total of 7,500 pounds of contaminated soil was processed through the CBC, of which 4,700 pounds were actual McColl waste. The materials that were processed included: unblended waste, waste blended with clean sand, and unblended waste "spiked" with carbon tetrachloride (CCL_4). The materials were processed without difficulty. Samples of the waste feed, fly ash, bed ash, and stack gas were taken by an EPA

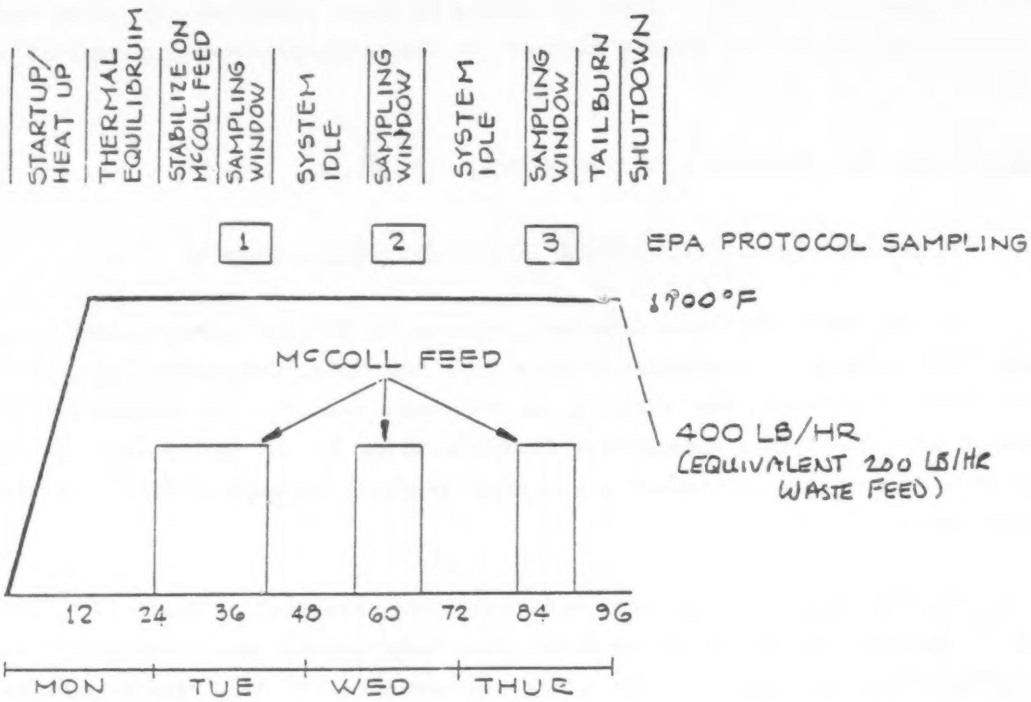

STARTUP/ HEAT UP
THERMAL EQUILIBRUIM
STABILIZE ON McCOLL FEED
SAMPLING WINDOW
SYSTEM IDLE
SAMPLING WINDOW
SYSTEM IDLE
SAMPLING WINDOW
TAILBURN
SHUTDOWN
1
2
3
EPA PROTOCOL SAMPLING
1900°F
McCOLL FEED
400 LB/HR
(EQUIVALENT 200 LB/HR WASTE FEED)
12
24
36
48
60
72
84
96
MON
TUE
WED
THUR

Fig. 6. McColl Treatability Study Test Sequence

contractor for extensive analysis. The samples are being analyzed for organic compounds, (including dioxins and furans), metals, criteria pollutants, and physical properties.

EPA has officially released preliminary data which has been checked to assure that it meets EPA standards and the complete demonstration test report will be available in August 1989. The results show organic material was effectively destroyed as exhibited by the destruction and removal efficiency (DRE) value shown in Table 2. No significant levels of hazardous organic compounds left the CBC system in the stack gas or remained in the bed and fly ash material, as shown in Table 3, which presents information on feed and residuals characteristics. The criteria pollutant and acid-gas release data obtained meet federal, state and South Coast Air Quality Management District (SCAQMD) requirements. Table 4 contains data on stack criteria pollutant and acid-gas emissions. Table 5 presents stack gas particulate loading data that are significantly below the federal requirement of 0.08 grains/dry standard cubic foot (corrected to 7% oxygen). The average particulate loading, however, is higher than the SCAQMD requirement of 0.002 grains/dscf. A Toxicity Characteristic Leaching Procedure (TCLP) test was performed on the McColl CBC ash. Arsenic, selenium, barium, cadmium, chromium, lead, mercury and silver leachabilities were found to be low and meet or exceed the federal requirements (40 CFR Part 268).

The EPA has concluded the test was successful based on the available data.

Transportable CBC Unit Field Demonstration Test

OES conducted a PCB-contaminated soil demonstration test burn at our Swanson River, Alaska remediation site project in September 1988, in accordance with a test burn plan prepared by OES and approved by the EPA Office of Toxic Substances. The test burn was conducted under witness of the EPA and the Alaska Department of Environmental Conservation (ADEC) at the remote Swanson River Alaska site on the Kenai peninsula. All required performance criteria were met, and OES has been granted a nation-wide PCB Disposal Operating Permit for its transportable 36-in. (i.d.) CBC unit.

TABLE 2

SITE/McCOLL TEST
DESTRUCTION AND REMOVAL EFFICIENCY (DRE)

Feed Rate	0.203	pounds per hour
Stack Emissions	0.000017	pounds per hour
DRE	99.992%	

average values using Carbon Tetrachloride (CCl_4)
as a performance indicator

TABLE 3

SITE/McCOLL TEST
FEED AND RESIDUALS CHARACTERISTICS

	Waste Feed	Fly Ash	Bed Ash	Stack Gas Emissions
ORGANICS (parts per million)				
Benzene	4.9	not detected	not detected	0.0008
Toluene	35.5	not detected	not detected	0.0015
Xylene	165.0	not detected	not detected	0.0015
Ethylbenzene	23.0	not detected	not detected	0.0004
1,1,1, Trichloroethane	not detected	not detected	not detected	0.0002
Naphthalene	30.2	not detected	not detected	0.0006
2-Methyl Naphthalene	34.5	not detected	not detected	0.0004
PHYSICAL PROPERTIES				
Sulfur (%)	4.4	3.6	0.9	--
pH	2.3	12.6	12.1	--
Density (pounds per cubic foot)	57.9	76.9	88.4	--
Heat Value (Btu/pound)	1387.0	--	--	--

"not detected" indicates a value below detection limits.

Organic feed and heat values are based on unblended waste averages. All other results are based on blended and unblended waste averages. Waste feed, fly ash and bed ash values are weight/weight. Stack gas emissions are volume/volume.

TABLE 4

SITE/McCOLL TEST
AIR EMISSIONS
(average values in pounds per hour)

Sulfur Oxides	(SO_x)	<2.0*
Nitrogen Oxides	(NO_x)	0.34
Carbon Monoxide	(CO)	0.12
Total Hydrocarbons	(THC)	0.007
Hydrochloric Acid	(HCl)	<0.01

*Further quantitation not possible due to SO_2 analyzer insensitivity in lower range.

TABLE 5

SITE/McCOLL TEST
PARTICULATE LOADINGS
(average values)

	Test Results	Permit Limits
gr/dscf	0.0038	0.08
mg/dscm	8.72	180.0
lb/hr	0.0242	not specified

gr/dscf	grains per dry standard cubic feet corrected to 7% oxygen
mg/dscm	milligrams per dry standard cubic meter

USE IN THE U.S.

The CBC technology has been recently applied in large scale at two site remediation projects that will treat over 80,000 tons of contaminated soil. OES has proven the effectiveness of transportable CBCs by locating and operating them cost-effectively in demanding environments. Every regulatory requirement for site operations has been met, and OES is consistently in compliance at both sites. The transportable CBCs have been operated in weather as cold as -40°F and as high as 110°F. The ruggedness of the units has been demonstrated by mobilizing and operating successfully in a remote and ecologically sensitive wildlife refuge. OES has maintained high levels of availability through the use of careful logistics planning that includes design factors, maintenance, and supply planning. A descriptive summary of OES' two major projects is given below.

PCB SITE REMEDIATION PROJECT

The ARCO Alaska Swanson River site is located within the Kenai Wildlife Refuge. PCB contamination was identified during site soil sampling conducted by the U.S. Fish and Wildlife Service in 1984. The contamination was an indirect result of a compressor explosion which occurred in 1972. Remediation activities were initiated by a voluntary "Order by Consent" signed by the site operator. The remediation is being conducted under the direction of the U.S. Fish and Wildlife Service, the Bureau of Land Management, and the Alaska Department of Environmental Conservation, with the concurrence of the U.S. Environmental Protection Agency Region X.

OES was selected for the remediation project because of demonstrated PCB destruction capabilities and the CBC combustion technology. OES' comprehensive site remediation workscope includes mobilization, on-site demonstration testing, excavation, contaminated vegetation clearing, incineration, contaminated water treatment, concrete and metal surface decontamination, demobilization, and site restoration.

The completion of the Swanson River project is scheduled for the end of 1991. Upon completion, over 70,000 tons of PCB-contaminated gravel/silt soil will have been treated. Figure 7 is a photograph of the Swanson River site.

FUEL OIL SITE REMEDIATION

For more than 50 years, a leaking underground storage tank at a cannery in Stockton, California contaminated surrounding clay soil with No. 6 fuel oil. OES was contracted by the site operator to remediate the site using one of its transportable 36"-in. (i.d.) CBCs. OES developed and is implementing a remediation plan that encompasses site characterization, demolition of tanks and buildings, installation and operation of water intercept wells, water treatment, soil excavation, stockpiling, CBC treatment, placement of slurried purified soil, and site and building restoration.

The excavation and backfilling is complete and the CBC thermal treatment of stockpiled soils is approximately 30% complete (June, 1989). Upon completion of the project later in 1989, over 11,000 tons of contaminated soil will have been treated. Following restoration, the site will have its full commercial value restored and it will be available for unrestricted use. Figure 8 is an overview photograph of the Stockton project site.

TREATMENT COSTS

OES offers a comprehensive range of services for the disposal of hazardous wastes, including pilot plant testing services, permit application and responses to reviews and comments, economic and technical evaluation of waste disposal alternatives, engineering design of CBC plants to meet customers' needs and specific waste characteristics, supply of a mechanically complete commercial CBC unit and supervision and staff for operation of the unit.

Site remediation costs are divided into three categories. The first category includes the direct and indirect costs for engineering design, base equipment cost, materials, foundation and installation labor to erect a

Fig. 7. Swanson River Project Site, Aerial Photo
(Fall - 1988)

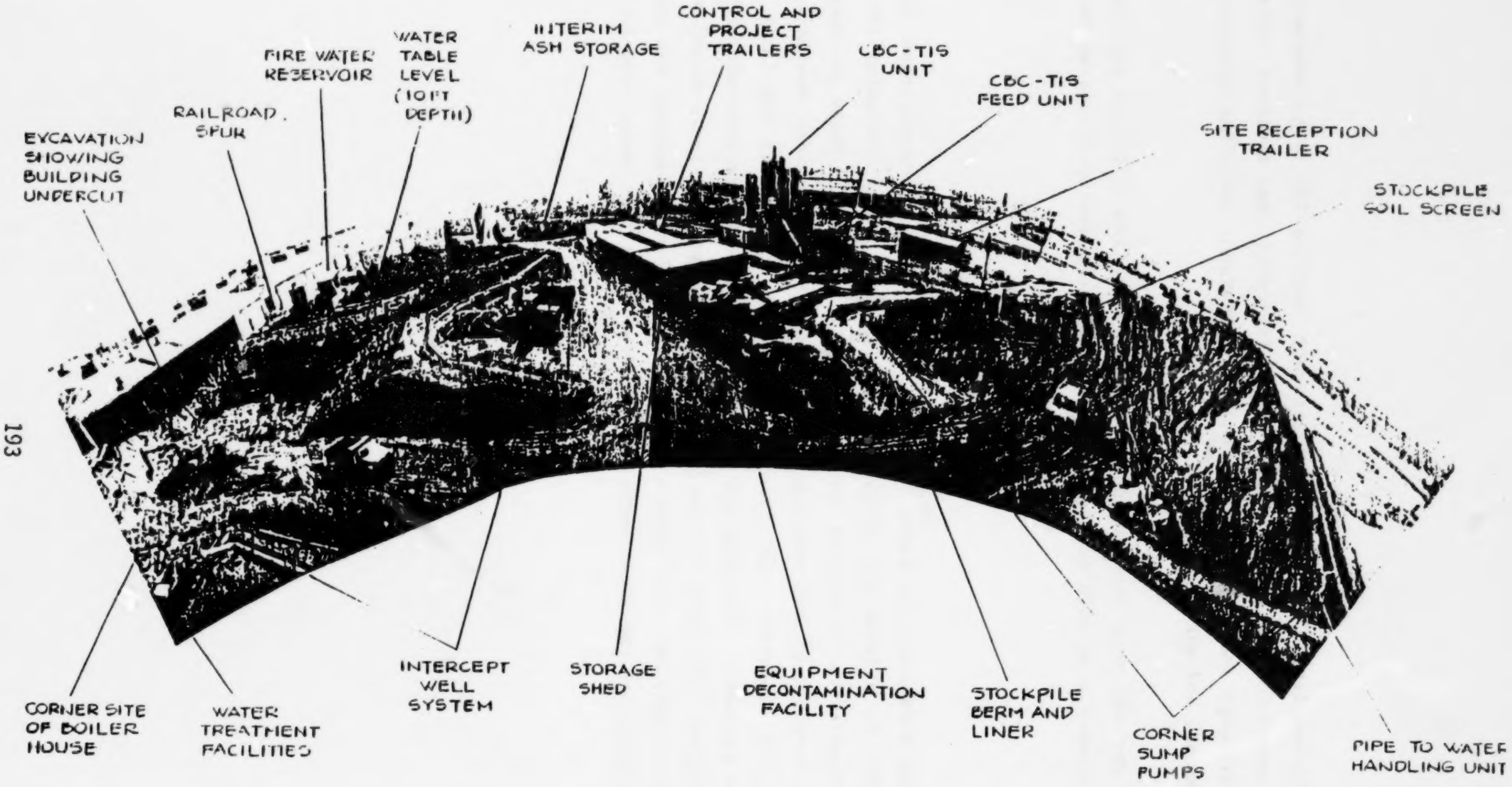

EXCAVATION SHOWING BUILDING UNDERCUT
RAILROAD SPUR
FIRE WATER RESERVOIR
WATER TABLE LEVEL (10FT DEPTH)
INTERIM ASH STORAGE
CONTROL AND PROJECT TRAILERS
CBC-TIS UNIT
CBC-TIS FEED UNIT
SITE RECEPTION TRAILER
STOCKPILE SOIL SCREEN
CORNER SITE OF BOILER HOUSE
WATER TREATMENT FACILITIES
INTERCEPT WELL SYSTEM
STORAGE SHED
EQUIPMENT DECONTAMINATION FACILITY
STOCKPILE BERM AND LINER
CORNER SUMP PUMPS
PIPE TO WATER HANDLING UNIT

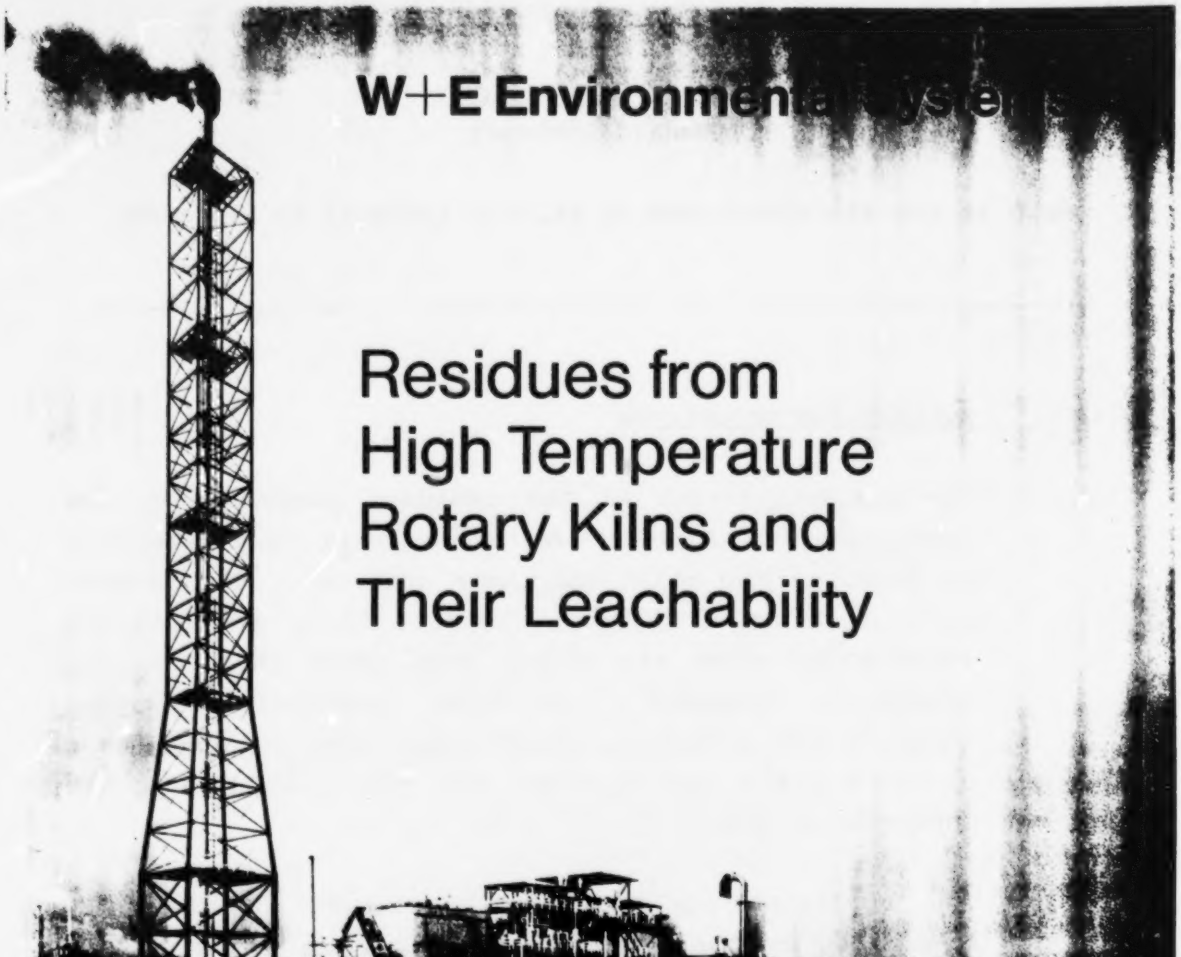
Fig. 8. Stockton Leaking Underground Storage Tank Remediation Site Photo

mechanically complete CBC. The second category includes CBC costs consisting of labor, materials, utilities, repair and maintenance, and indirect costs. The third category includes material handling operations including excavation, feed processing, and ash disposal.

Costs for CBC soil remediation typically range from $100-$300 per ton depending primarily on soil moisture content and the quantity of wastes to be processed.

SUMMARY

OES has developed CBC waste treatment technology and demonstrated its applicability in private and government sponsored programs including the Superfund Innovative Technology Evaluation (SITE) program. Based on this systematic development and testing, modular CBC units have been designed, fabricated and deployed. CBC treatment is being utilized in two large remediation projects. Treating contaminated soil in a CBC is cost-effective, highly efficient, and meets all performance and operation criteria established by regulatory agencies. The Ogden Corporation, OES' parent company, has made a major commitment to the site remediation business with four units soon to be operating.



W+E Environmental Systems

Residues from High Temperature Rotary Kilns and Their Leachability

BY

RONALD SCHLEGEL

HELD AT THE EPA CONFERENCE IN ATLANTA

JUNE 19–21, 1989

Residues from High-Temperature Rotary Kilns and Their Leachability

by

Ronald Schlegel

Held at the EPA Conference in Atlanta (June 19 to 21, 1989)

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1. Motives and Objectives

The characteristics of the residues generated by the combustion of hazardous waste obviously vary depending on where in the plant they were obtained. The largest portion of solid residues (roughly 80 %) are obtained immediately after the rotary kiln below the secondary combustion chamber. In high temperature systems slagging rotary kilns), these slags have the appearance of black glass, and it seems that they also possess the poperties of glass.

The remaining residues are discharged in the form either of boiler ash, filter cakes or filter dust, depending on the individual plant design.

Since the largest portion of all residues are obtained in the form of slags, we wanted to investigate under normal industrial operating conditions whether the composition of the slags allows for normal land disposal or even recycling.

We have been repeatedly approached in this matter, particularly by American firms who are interested in this question given the much tighter economic environment and the stringent liability regulations in the U.S. The slag leachability tests were consequently carried out by an EPA licensed laboratory.

The object of these tests was on the one hand to investigate the composition and leachability of the slags and on the other hand to obtain experimental results on the material flow under different waste composition conditions.

2. The Plant at Rijnmond (Netherlands)

The W+E rotary kiln process line of AVR-Chemie's hazardous waste incineration plant at Rijnmond took up operation in 1987 and now handles about 50,000 mt of waste a year. The plant consists of a high-temperature rotary kiln, a secondary combustion chamber, a steam boiler to recover the waste-generated heat and to cool down the flue gases prior to their treatment in a wet flue gas treatment system (Figs. 1 to 3, Table 1).

Since its purpose is to handle hazardous waste from all over the Netherlands, the plant has to cope with the entire spectrum of hazardous waste, ranging from unpacked and packed waste (200,000 barrels a year) to contaminated soil, liquid waste of any composition, sludges and clinical wastes. Moreover, ARV-Chemie is the only plant in the Netherlands licensed to incinerate PCB-containing wastes.

3. The Tests

The tests were carried out in cooperation with AVR-Chemie and our US licensee Combustion Engineering in September 1988.

Fig. 4 and Tables 2 to 5 show the sampling and measuring points that were used during the tests and whose data were recorded so that reliable energy and mass balances could be established.

The slag and ash samples were extracted every 15 minutes and mixed to representative samples, then immediately packed and dispatched to the US for the leachability tests.

The specified and analysed menu was fed four hours before the tests so that the plant would have reached a steady state condition by the time a series of measurements begins. This precaution ensures moreover that the slags and ashes are actually generated by the analysed waste samples.

Due to the large variety of waste--particularly solid waste--the plant has to process, we were forced to run the tests on a trace method basis. We ensured that the input contained a sufficient amount of the particular waste material in which we were interested. Otherwise, the plant was operated under normal commercial conditions.

The following test runs of different waste flows were executed (Table 6):

Test # 1

Without barrels; high organic content:
Apart from the "regular" contaminants, the waste mixture contained the following:

Chlorine:	335 kg/h
Fluorine:	60 kg/h
Sulphur compounds:	18 kg/h

Test # 3

High content of inert matter containing PCB

PCB	14 to 15 kg/h

Test # 4

High metal content (large number of barrels):
Apart from the "usual" materials, the waste mixture contained the following:

Heavy metals

Class I (Hg, Cd, Tl)	1,887 g/h
Class II (Ag, Co, Ni, Se, Te)	2,352 g/h
Class III (As, Pb, Cr, Cu, Mo, Zn, Rh, Va, Sn)	16,364 g/h
Total amount:	20,603 g/h

During all tests, the plant was operated under normal operating conditions and did not deviate from the usual, commercial operations. The operating parameters of all three test runs are given in Table 7.

The leachability tests were carried out according to the following three methods:

- Toxicity Test (EPA SW 846, Method 1310)
  Water is added to the sample and a pH of 5.0 ± 0.2 is maintained. Extraction Procedure Toxicity (EP-TOX) analytes are given in Table 8.

- Toxicity Characteristics Leaching Procedure (TCLP)
  In contrast to the EP-TOX test, a special extraction fluid is used. The maximum allowable concentrations are shown in Table 9.

- o **Total Extractable Metals**

  Here, the metals are solved by acids and analysed by means of argon plasma spectroscopy.

4. Results (Figs. 5.1 to 6.3)

4.1 Material flow

The consideration of all tests revealed that 90 % of the solids input volume is discharged in the form of slags, whereas only 10 % verge into other output flows.

Analyses of individual heavy metal flows in the plant revealed a number of interesting results, though there is obviously nothing new to be said about mercury; 92 % was determined in the scrubber (scrubbing liquid) and 7.2 % in the flue gas.

Much more interesting are the cadmium analyses since they revealed a total output that was about 3.7 times higher than the measured input. These tests proved once again that the major part of all cadmium in the waste is not present in its pure form, but in plastics, paints, and other materials.

The analysis results showed that the nickel, cobalt, chromium and copper contained in the slag are mainly of a form that does not allow leaching.

4.2 Leachability Tests

The leachability tests according to the TCLP Method show that all values fall short of the threshold limits by at least a factor of 100.

5. Conclusion

The TCLP tests carried out the slag samples obtained from a high temperature rotary kiln incineration system show that the leachability of heavy metals of this slag is considerably lower than the threshold limits for landfill disposal that are in force in the U.S.

The fact that all these results were achieved with regular residues and under normal commercial plant operation conditions indicates that there is a probability that this slag may be delisted. Although any delisting would have to take place on a case to case basis, there are enormous potential advantages. For instance, the sanitary landfill disposal costs for the largest portion of all residues--up to 80 %--could be drastically reduced and, even more important, the potential liability risk of this slag is not comparable to that of hazardous residues.

These tests are obviously just a beginning; further programs will be required to build a data base on the disposal of slag obtained from these incineration systems. They did, however, prove again that the high-temperature rotary kiln technology as applied in Europe is the best method of incinerating large amounts of the entire range of hazardous wastes. In Europe, such incinerators have to process hazardous waste of entire countries, or at least vast regions. Therefore, they typically have large capacities of up to 50,000 mt and handle e.g. 55 gallon metal drums, sundry package types and other solid waaste, sludges, slurries, liquids, aqueous waste, etc.

It is of course essential that the residues leaving the plant be not as toxic as the input and that the volume be reduced. The tests proved that these requirements were met, at least for the largest portion of these residues.

6. Bibliography

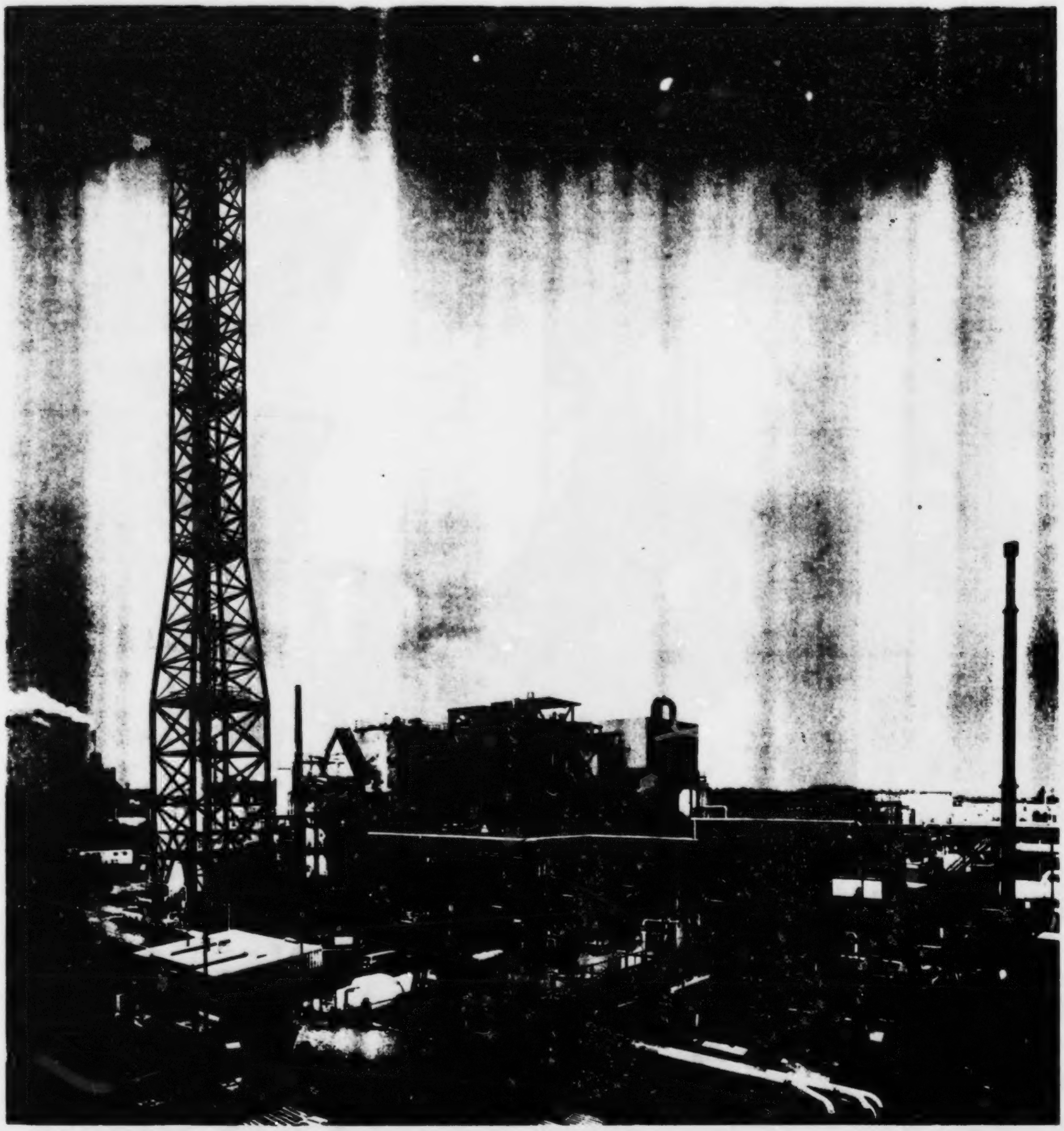
(1) TCLP Procedure, Part II, Environmental Protection Agency, 40 CFR Part 260 et al.

(2) EP-TOX (Method C004), U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods," SW-846 (1980), Section 7.

RIJNMOND FACILITY, NETHERLANDS

Fig. 1

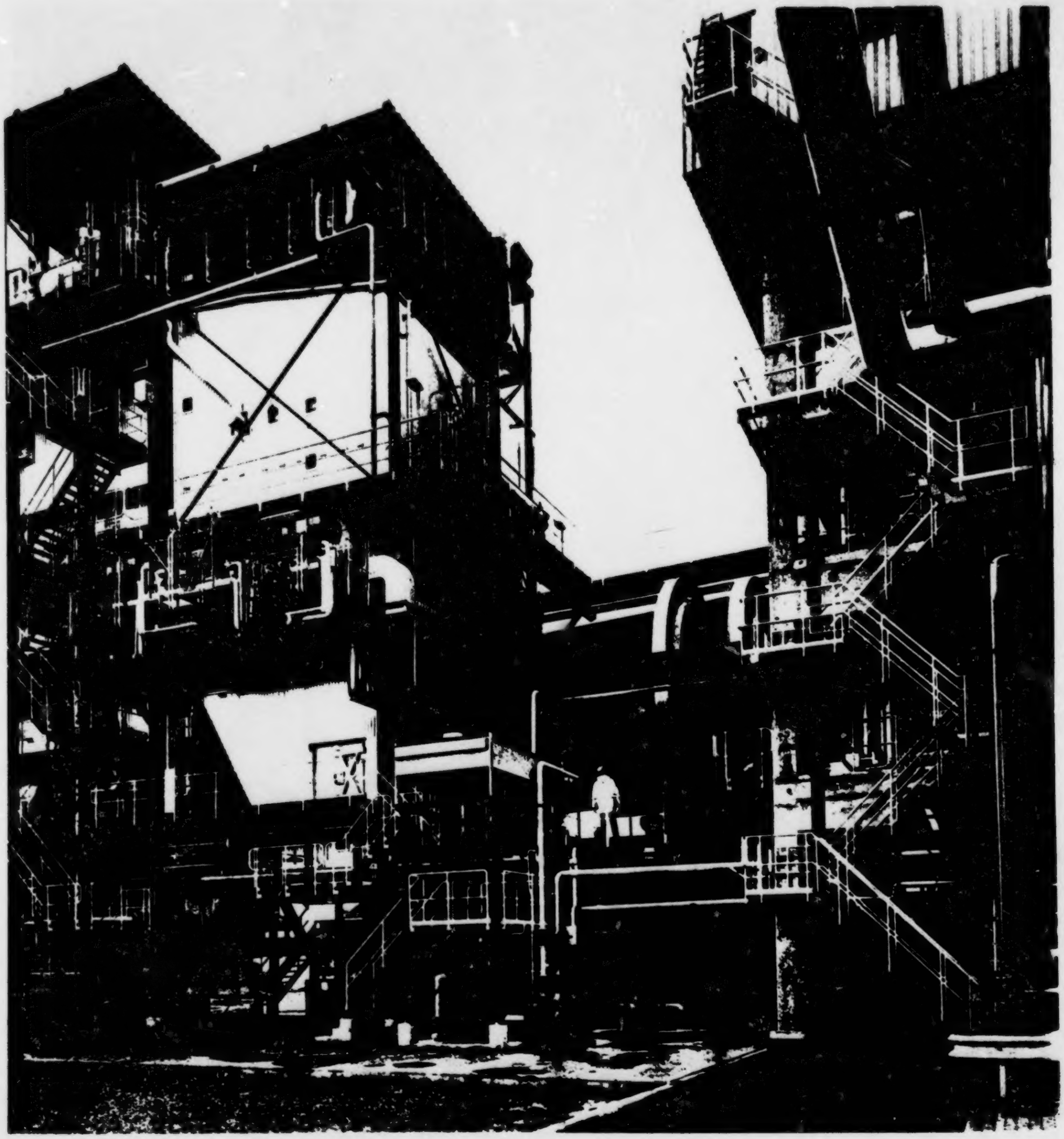
ANLAGE RIJNMOND, HOLLAND



RIJNMOND FACILITY

Fig. 2

ANLAGE RIJNMOND



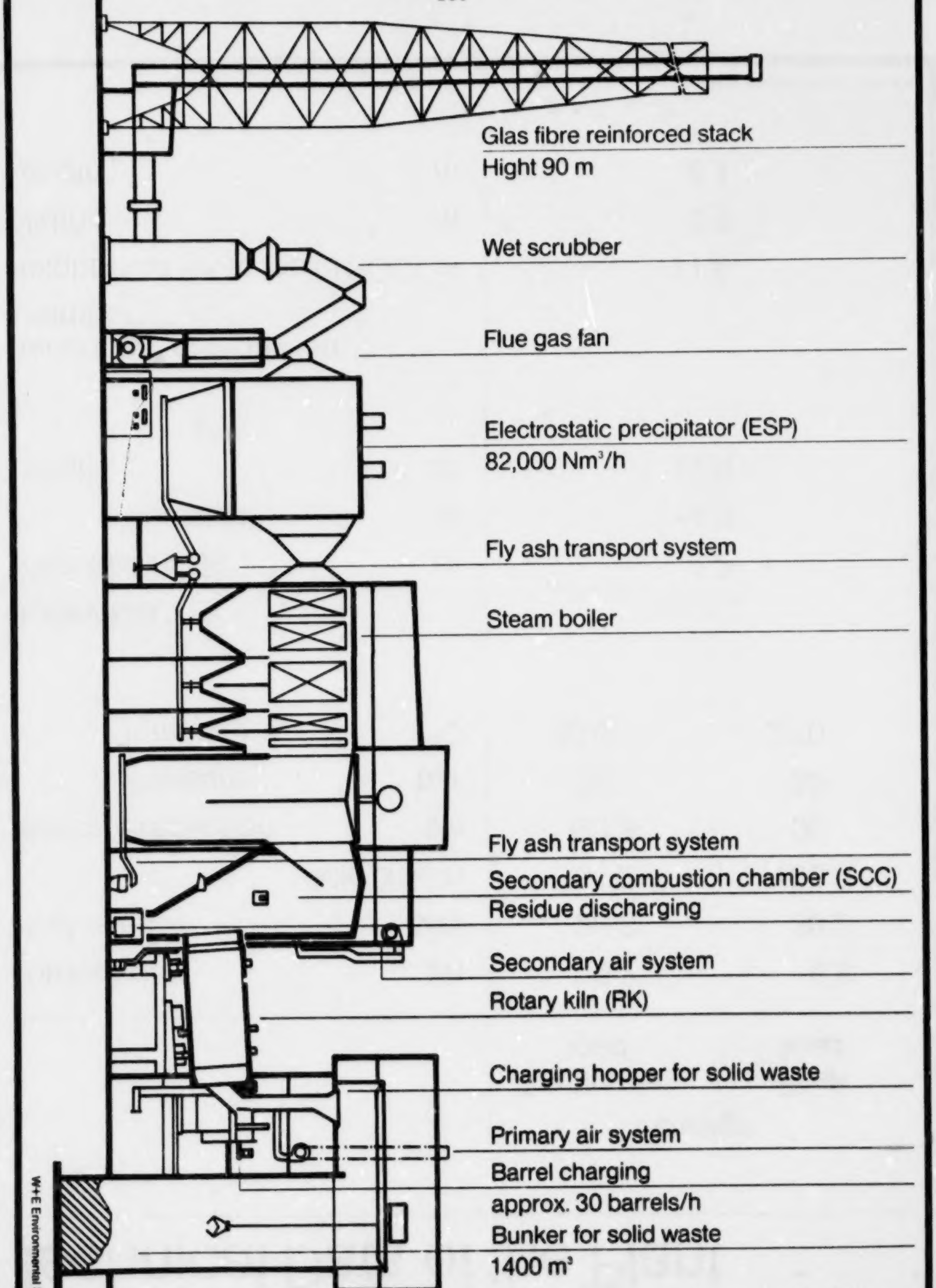

Glas fibre reinforced stack
Hight 90 m
Wet scrubber
Flue gas fan
Electrostatic precipitator (ESP)
82,000 Nm³/h
Fly ash transport system
Steam boiler
Fly ash transport system
Secondary combustion chamber (SCC)
Residue discharging
Secondary air system
Rotary kiln (RK)
Charging hopper for solid waste
Primary air system
Barrel charging
approx. 30 barrels/h
Bunker for solid waste
1400 m³
W+E Environmental Systems

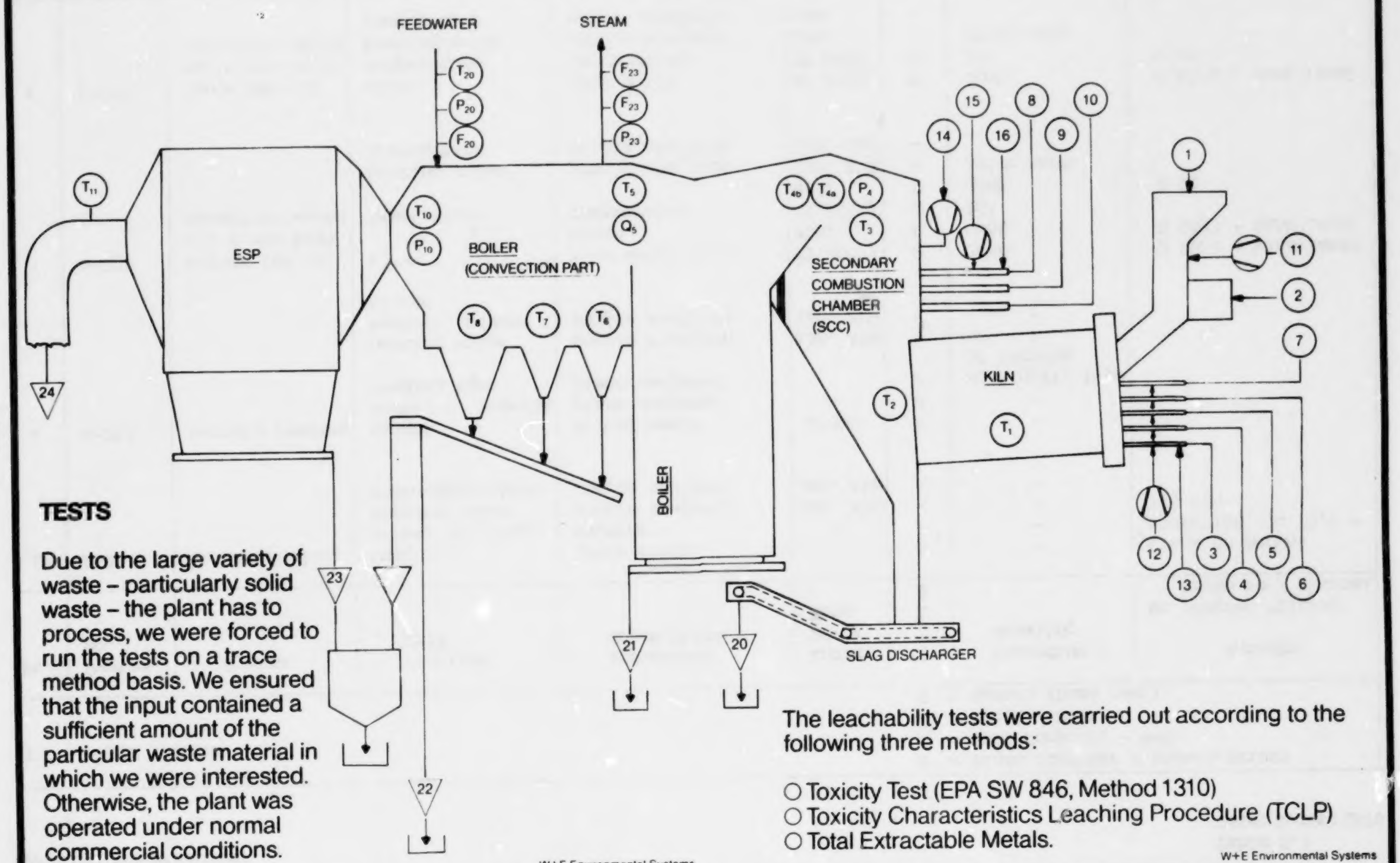
Fig. 3

Table 1

Technical Data of the Plant

		Design	
		Continuous load	Peak load
Throughput	t/h	6.2	6.8
Heat release	MW	23.8	30.2
	Mio BTU/h	81.2	103.0
Steam: Production	t/h	23.3	30
Pressure	bar	30	30
Temperature	°C	370	370
Rotary kiln:			
Diameter inside	m	4.2	
outside	m	4.9	
Length	m	12.0	
Secondary combustion chamber:			
Height (Axis RK to top of SCC)	m	11.6	
Width	m	6.6	
Length	m	6.1	

W+E Environmental Systems


FEEDWATER
STEAM
T_{20}
P_{20}
F_{20}
F_{23}
F_{23}
P_{23}
T_{11}
ESP
T_{10}
P_{10}
BOILER
(CONVECTION PART)
T_5
Q_5
T_8
T_7
T_6
T_{4b}
T_{4a}
P_4
T_3
T_2
SECONDARY
COMBUSTION
CHAMBER
(SCC)
BOILER
KILN
T_1
SLAG DISCHARGER
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
20
21
22
23
24

TESTS

Due to the large variety of waste – particularly solid waste – the plant has to process, we were forced to run the tests on a trace method basis. We ensured that the input contained a sufficient amount of the particular waste material in which we were interested. Otherwise, the plant was operated under normal commercial conditions.

W+E Environmental Systems

The leachability tests were carried out according to the following three methods:

○ Toxicity Test (EPA SW 846, Method 1310)
○ Toxicity Characteristics Leaching Procedure (TCLP)
○ Total Extractable Metals.

W+E Environmental Systems

SAMPLING AND MEASURING

Table 2.1
Date: August 1988

I WASTE FEEDING

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
1	A-251	solids feeding	weight	crane scale	-	S	-	Crane on manual operation, ca. 5,0 - 7,5 t/h
			number of lifts	counter	-	S	-	
			heating value	sample analysis	lab. AVR	-	-	
			main composition	sample analysis	lab. AVR	-	-	
2	A-252	barrels feeding	weight	barrel scale	W8350	P	-	
			number of barrels	plant computer	-	P	-	
			feeding time	plant computer	-	P	each diff. type of barrels	
			heating value	sample analysis	lab. AVR	-	"	
			content, composition	sample analysis	lab. AVR	-	-	
3	A-201	burner for oil no. 6 and high calorific waste	flow	flow meter no.6/ waste	FI 8001/ 8002	P P	cont. cont.	G 95/2 + tank level G 95/3 + tank level
			temperature	thermometer	TI 8001/ 8002	L P	15' cont.	G 00
			heating value	sample analysis	lab. AVR	-	15'or cont.	
			composition	sample analysis	lab. AVR	-		
4	A-202	lance for oil no. 6 and high calorific waste	flow	flow meter	FI 8003	P	cont.	G 95/4 + tank level
			temperature	thermometer	TI 8003	P	15'	G 00
			heating value	sample analysis	lab.	-	15'or cont.	
			composition	sample analysis	lab.	-	-	

SAMPLING AND MEASURING

Table 2.2
Date: August 1988

I WASTE FEEDING

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
5	A-203	burner for med.	flow	flow meter	FI 8004	P	cont.	G 95/5
		calorifc waste	temperature	thermometer	TI 8005	P	15'	
			heating value	sample analysis	lab. AVR	-	15'	
			composition	sample analysis	lab. AVR	-	-	
6	A-204	lance for	flow	level difference	-	P	15'	tank level measurem.
		pasteous waste	temperature	thermometer	TI 8002	P	cont.	G 00
			heating value	sample analysis	lab. AVR	-	15'or cont.	
			composition	sample analysis	lab. AVR	-	-	
7	A-207	lance for	flow	flow meter	FI 8009	P	-	G 99/5, during test
		polymerized	temperature	thermometer	TI 8006	-	-	not in operation
		waste	heating value	sample analysis	lab. AVR	-	-	
			composition	sample analysis	lab. AVR	-	-	
8	A-206	burner SCC for	flow	flow meter	FI 8005/	P	cont.	G 95/6 + tank level
		oil no. 6 and			8006	P	cont.	G 95/7 + tank level
		high calorific	temperature	thermometer	TI 8007/	L	15'	G 00
		waste			8008	P	cont.	
			heating value	sample analysis	lab. AVR	-	15'or cont.	
			composition	sample analysis	lab. AVR	-		

Table 2.3
Date: August 1988

I WASTE FEEDING

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
9	A-205A	lance for low calorific waste (waste water)	flow	flow meter	FI 8007	P	-	G 94/2 + tank level
			temperature	thermometer	TI 8009	P	cont.	
			heating value	sample analysis	lab.	-	15'or cont.	
			composition	sample analysis	lab.	-	-	
10	A-205B	lance for low calorific waste (waste water)	flow	flow meter	FI 8008	P	-	G 95/1 + tank level
			temperature	thermometer	TI 8010	P	15'or cont.	
			heating value	sample analysis	-	-	15'	
			composition	sample analysis	-	-	-	

SAMPLING AND MEASURING

Table 3
Date: August 1988

II AIR FLOW

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
11	K-251	primary air	flow	annubar	F 8100	P/T	cont.	G 94/3
T	K-251	primary air	temperature	PT-100	T 8102	T	cont.	
12	K-255	cooling air	flow	pitot or anemometer	W+E/AVR	L	1 x	travers measurement (ca. 2000 m3/h)
13	K-	burner air	flow	pitot	W+E	L	cont.	
14	K-252	secondary air	flow	annubar	F 8103	P/T	cont.	G 94/4
15	K-256	conding. air	flow	pitot	-	L	1 x	travers measurement (ca. 2000 m3/h)
16	K-	burner air	flow	pitot	W+E	L	cont.	

III SLAG, ASH AND FLUE GAS

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
20	A-266	slag discharger	tot. weight	-	-	-	-	See procedure for slag sampling
			repr. sample	-	-	-	15′	Sample analysis:CE
21	X-250	boiler ash radiation part discharger	tot. weight	-	-	-	-	
			repr. sample	-	-	-	cont.	mixed - representative sample Sample analysis:CE
22	X-251	boiler ash conv. part discharger	tot. weight	-	-	-	-	sampled through the emergency opening with a special installation.
			repr. sample	-	-	-	cont.	- mixed - repr. sample Sample analysis:CE
23	X-252	ESP-ash	tot. weight	-	-	-	-	
			repr. sample	-	-	-	cont.	Sample analysis:CE

Table 4.2
Date: August 1988

III SLAG, ASH AND FLUE GAS

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
24		flue gas to gas cleaning system	flow	-	-	L	cont.	
(Q5)			CO-content	Siemens-Ultramat	QI 8101	P	cont.	G 96/2
			HCL	-	AVR	L	cont.	Analysis: AVR
			HF	-	AVR	L	cont.	Analysis: AVR
			H_2O	-	AVR	L	cont.	Analysis: AVR
			Dust-content	-	AVR	L	cont.	Analysis: CE
			Heavy metals in the gas	-	AVR	L	cont.	Analysis: CE
			O_2-content	-	AVR	L	cont.	Analysis: AVR
			CO-content	-	AVR	L	cont.	Analysis: AVR
		flue gas to stack	SO_2	Sick GM 21	QI 8205			G 96/5
			CO		QI 8208	P	cont.	

Table 5.1
Date: August 1988

IV PROCESS AND CONTROL MEASUREMENTS

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
T1	F-251	kiln shell	wall temperature	local thermometer	T 8091/ 94/97	L	1 x	
T2	F-251	kiln	slag temperature	pyrometer	TI 8106	P/T	cont.	G 90/1
T3	F-252	SCC wall	wall temperature	local thermometer	T 8054/ 55	L	1 x	
T4a	F-252	SCC outlet	gas temperature	thermo couple	TI 8107	T/P	cont.	G 90/2
T4b	F-252	SCC outlet	gas temperature	pyrometer	TI 8108	P	cont.	G 90/3
P4	F-252	SCC outlet	gas pressure	pressure transm.	PI 8110	P/T	cont.	G 92/3
T5a	H-251	boiler-radiation-part outlet	gas temperature	thermo couple	TI 8109	P/T	cont.	G 90/4
Q5	H-251	boiler-radia tion-part outlet	CO Vol-%	CO-test	QI 8101	P/T	cont.	G 96/2
T6	T-253	ash-hopper	gas temperature	thermometer	T 8073	L	30′	
T7	T-254	ash hopper	gas temperature	thermometer	T -	L	30′	
T8	T-255	ash hopper	gas temperature	thermometer	T -	L	30′	

Table 5.2
Date: August 1988

IV PROCESS AND CONTROL MEASUREMENTS

P = Plant Computer / Screen Prints
T = Test Computer - W+E
L = Local / Rack
S = Screen (hand rec.)

Pt.	System No.	System	Required Info	Instrument Check Point	Instr. No. / Resp.	P T L S	Recording / Sampling	Remarks G: (Screen Prints) Group no / channel
T10	T-	boiler outlet	gas temperature	PT-100	TI 8110	P/T	cont.	G 90/5
P10	T-	boiler outlet	gas pressure	pressure transm.	PI 8112	P	cont.	
P20	-	feed water	pressure	pressure transm.	PI 8118	T	cont.	
T20	-	feed water	temperature	thermometer	TI 8114	P/T	cont.	
F20	-	feed water	flow	annubar	FI 8101	P	cont.	G 94/6
P23	-	steam	pressure	pressure transm.	PI 8124	T	cont.	
T23	-	steam	temperature	thermometer	TI 8123	P	cont.	G 101/4
F2B	-	steam	flow	annubar	FI 8102	P	cont.	G 94/5
T11	-	fuel gas at ESP outlet	temperature	PT-100	TI 8207	T	cont.	
-	-	cooling water	flow temp. difference	pump characteristic thermometer	- -	- -	1 x 1 x	
-	-	cooling air RK	flow	anemometer	-	-	1 x	

TEST #1 High organic content

Tank Number	Bunker Number	Lance Number	Input kg/h	Inputs [%] of Cl	F	P	S
517		203	487	24,70	11,20	-	1,20
	315	Solids	1500	0,10	0,04	-	0,10
513		202	2958	6,80	0,18	-	0,30
512		205	582	2,10	0,04	-	0,30
	Total		5527	6,06	1,10	-	0,33

TEST #3 PCB content in waste

Tank Number	Bunker Number	Lance Number	Input kg/h	Inputs [%] of Cl	F	P	S
	251	Barrels	2100	0,10	0,05	-	0,20
	252	Drums	356	0,20	0,01	-	0,20
		Polymer	483	0,10	0,04	-	0,10
513		201	2475	1,78	0,34	-	0,10
518		203	920	0,10	0,01	-	0,30
	Total		6334	0,76	0,15	-	0,17

TEST #4 High heavy metal content in waste

Tank Number	Bunker Number	Lance Number	Input kg/h	Inputs [%] of Cl	F	P	S
	310	Solids	850	0,20	0,01	-	0,20
		Drums	1446	0,30	1,31	-	0,30
		Polymer	551	0,10	0,04	-	0,10
514		201	2465	6,90	0,13	-	0,70
512		203	2100	2,10	0,03	-	0,70
	Total		7412	2,98	0,31	-	0,52

SOLIDS

Test #	Input = 100 % calcul. kg/h	Output of Slag kg/h	wet-ash kg/h	Boiler-ash kg/h	ESP-ash kg/h	Rawgas-concentr. mg/Nm^3	Volume-flow Nm^3/h
1	1164	1020	8	44	89	37	68300
3	1727	1590	20	68	48	19	66800
4	1005	900	9	15	75	88	70200
Mean	1299	1170	12	42	71	48	68433

Amount [kg/h]				Metal input [g/h]			
Cl	F	P	S	Hg	Cd	Tl	As
120,29	54,54	-	5,84	0,10	0,49	-	-
1,50	0,60	-	1,50	17,85	1,50	-	-
201,14	5,32	-	8,87	1,51	2,96	-	-
12,22	0,23	-	1,75	0,50	2,04	-	-
335,16	60,70	-	17,96	19,96	6,98	-	-

Amount [kg/h]				Metal input [g/h]			
Cl	F	P	S	Hg	Cd	Tl	As
2,10	1,05	-	4,20	0,63	2,10	-	-
0,71	0,04	-	0,71	0,06	0,36	-	-
0,48	0,19	-	0,48	0,06	0,48	-	-
44,06	8,42	-	2,48	2,65	2,48	-	-
0,92	0,09	-	2,76	2,39	0,92	-	-
48,27	9,79	-	10,63	5,80	6,33	-	-

Amount [kg/h]				Metal input [g/h]			
Cl	F	P	S	Hg	Cd	Tl	As
1,70	0,09	-	1,70	0,81	0,85	-	-
4,34	18,94	-	4,34	1832,08	32,54	-	-
0,55	0,22	-	0,55	0,17	0,55	-	-
170,09	3,20	-	17,26	2,02	2,47	-	-
44,10	0,63	-	14,70	3,86	11,55	-	-
220,77	23,08	-	38,54	1838,94	47,95	-	-

Rawgas dust kg/h	Gas-humidity vol-%	Slag percent from solids %
2,53	9,2	87,66
1,27	10,9	92,05
6,18	8,3	89,54
3,3	9,5	89,75

HAZARD GASES		
HCl tr. Rawgas-conc. calcul. mg/Nm^3	HF tr. Rawgas-conc. calcul. mg/Nm^3	SO2 tr. Rawgas-conc. calcul. mg/Nm^3
5509,50	1021,59	574,43
823,94	171,01	352,95
3501,90	374,84	1189,26

Co	Ni	Sb	Pb	Cr	Cu	Sn	Ba
15,10	40,42	-	46,27	4,87	4,87	60,88	-
82,50	222,00	-	258,00	27,00	322,50	331,50	-
283,97	760,21	-	854,86	94,66	6321,25	1990,73	-
39,58	81,48	-	91,37	9,89	72,17	122,22	-
421,14	1104,11	-	1250,50	136,42	6720,78	2505,33	-

Co	Ni	Sb	Pb	Cr	Cu	Sn	Ba
210,00	420,00	-	420,00	210,00	1680,00	630,00	-
35,60	35,60	-	35,60	35,60	35,60	35,60	-
48,30	48,30	-	48,30	48,30	48,30	48,30	-
247,50	247,50	-	247,50	247,50	247,50	247,50	-
92,00	92,00	-	276,00	92,00	828,00	184,00	-
633,40	843,40	-	1027,40	633,40	2839,40	1145,40	-

Co	Ni	Sb	Pb	Cr	Cu	Sn	Ba
85,00	85,00	-	85,00	85,00	765,00	85,00	-
144,60	144,60	-	2169,00	144,60	144,60	144,60	-
55,10	110,20	-	110,20	55,10	440,80	165,30	-
246,50	246,50	-	246,50	246,50	1232,50	493,00	-
210,00	210,00	-	420,00	210,00	210,00	210,00	-
741,20	796,30	-	3030,70	741,20	2792,90	1097,90	-

Ag	Se	Be	Zn	Mo	input of analysed heavy metals
65,75	4,87	–	4,87	35,06	g/h
360,00	15,00	–	27,00	111,00	
1236,44	29,58		94,66	381,58	
132,11	5,82	–	9,89	58,78	
1794,30	55,27	–	136,42	586,43	14737,65

Ag	Se	Be	Zn	Mo	input of analysed heavy metals
210,00	21,00	–	7140,00	210,00	g/h
35,60	3,56	–	35,60	35,60	
48,30	4,83	–	48,30	48,30	
247,50	24,75	–	247,50	247,50	
92,00	9,20	–	1472,00	92,00	
633,40	63,34	–	8943,40	633,40	17408,07

Ag	Se	Be	Zn	Mo	input of analysed heavy metals
85,00	8,50	–	255,00	85,00	g/h
144,60	14,46	–	2892,00	578,40	
55,10	5,51	–	1873,40	55,10	
246,50	24,65	–	2711,50	246,50	
210,00	21,00	–	2,10	2,10	
741,20	74,12	–	7734,00	967,10	20603,51

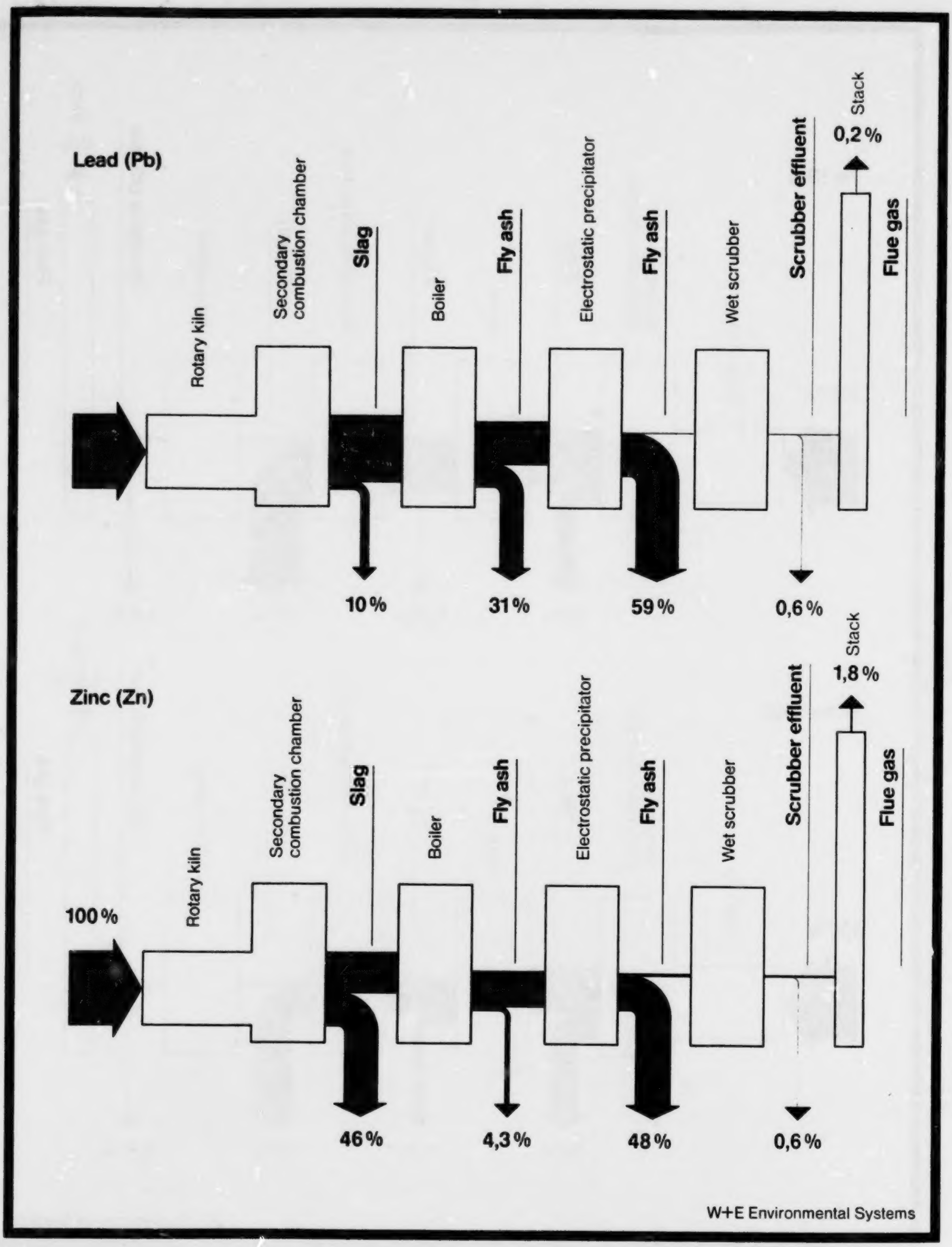
Table 7

Operating Data at Slag Tests

Measurable Variable		Test 1	Test 3	Test 4
Temperature rotary kiln	°C	1255	1290	1260
Temperature secondary combustion chamber	°C	1076	1250	1100
Boiler outlet	°C	250	250	250
Steam temperature	°C	379	391	391
Steam pressure	bar	30	30	30
Steam production	t/h	27.9	33.5	29.2
Volume flow	m^3/h (N, f)	75,200	74,300	76,500
Oxygen content	% Vol.	8.7	6.3	7.5
Gas humidity	% Vol.	9.2	10.9	8.3

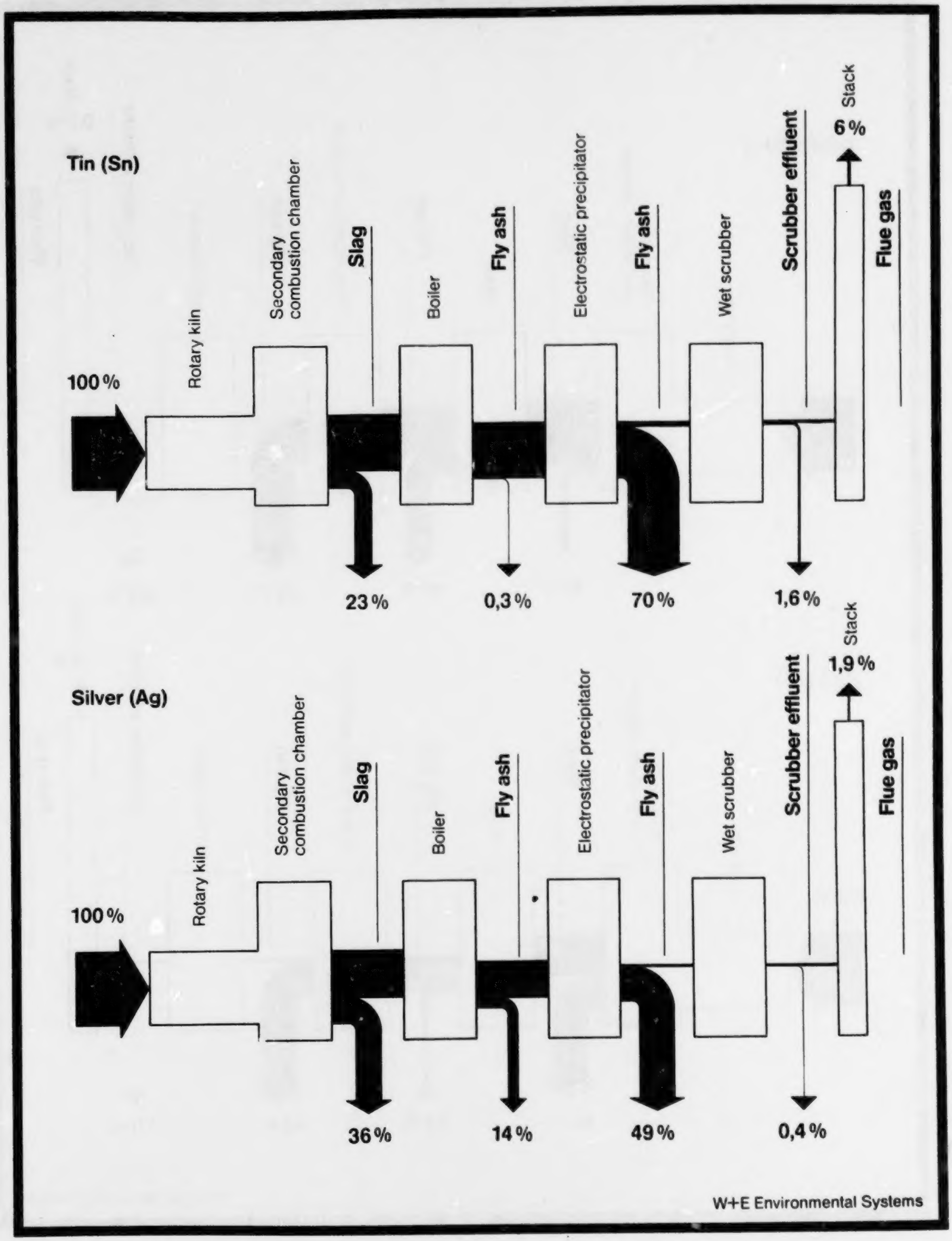
W+E Environmental Systems

Fig. 5.1

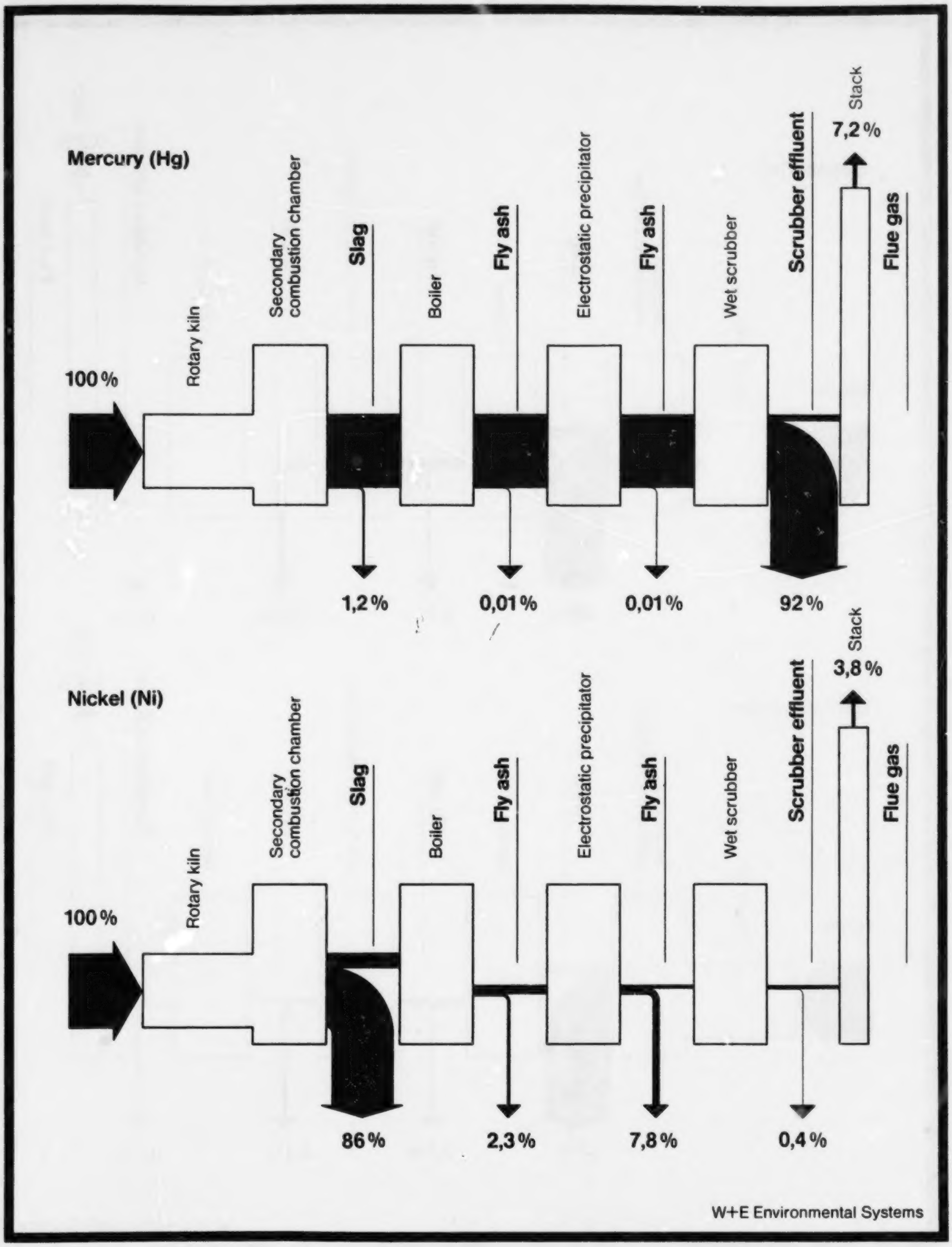

Lead (Pb)
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
0,2 %
Flue gas
10 %
31 %
59 %
0,6 %
Zinc (Zn)
100 %
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
1,8 %
Flue gas
46 %
4,3 %
48 %
0,6 %

W+E Environmental Systems

Fig. 5.2

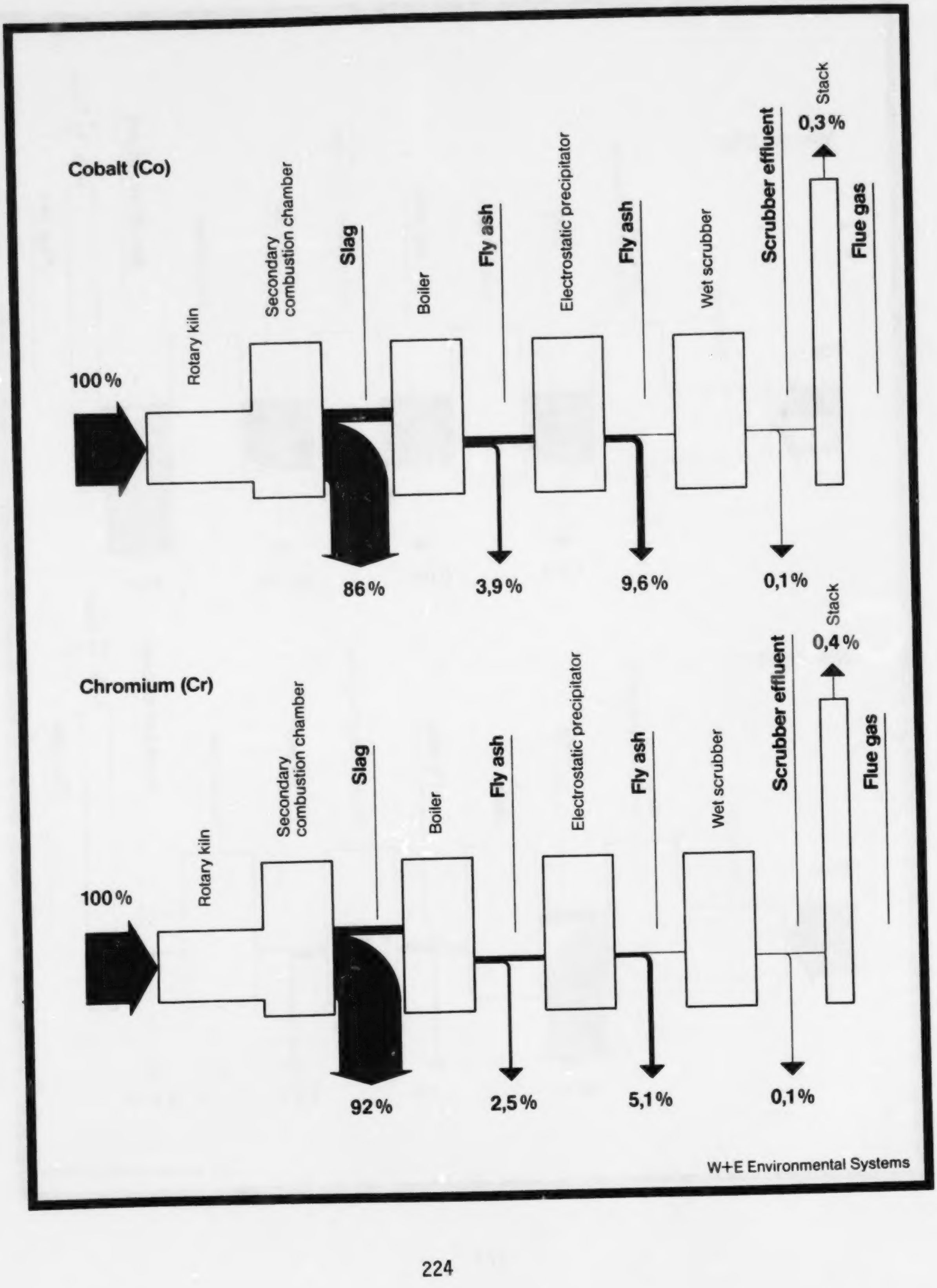

Tin (Sn)
100 %
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
6 %
Flue gas
23 %
0,3 %
70 %
1,6 %
Silver (Ag)
100 %
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
1,9 %
Flue gas
36 %
14 %
49 %
0,4 %

W+E Environmental Systems

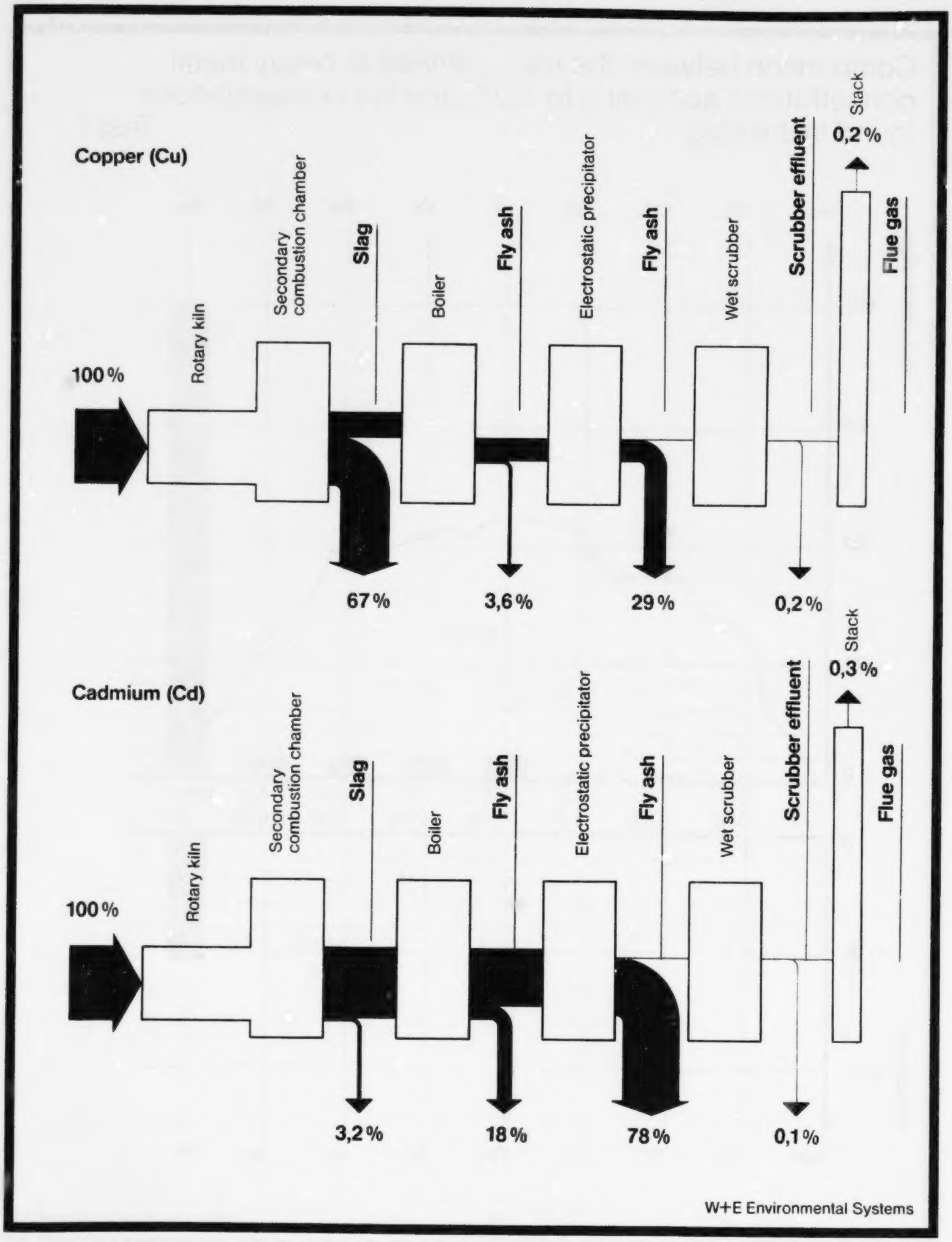

Mercury (Hg)
100 %
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
7,2 %
Flue gas
1,2 %
0,01 %
0,01 %
92 %
Nickel (Ni)
100 %
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
3,8 %
Flue gas
86 %
2,3 %
7,8 %
0,4 %

W+E Environmental Systems

Fig. 5.4

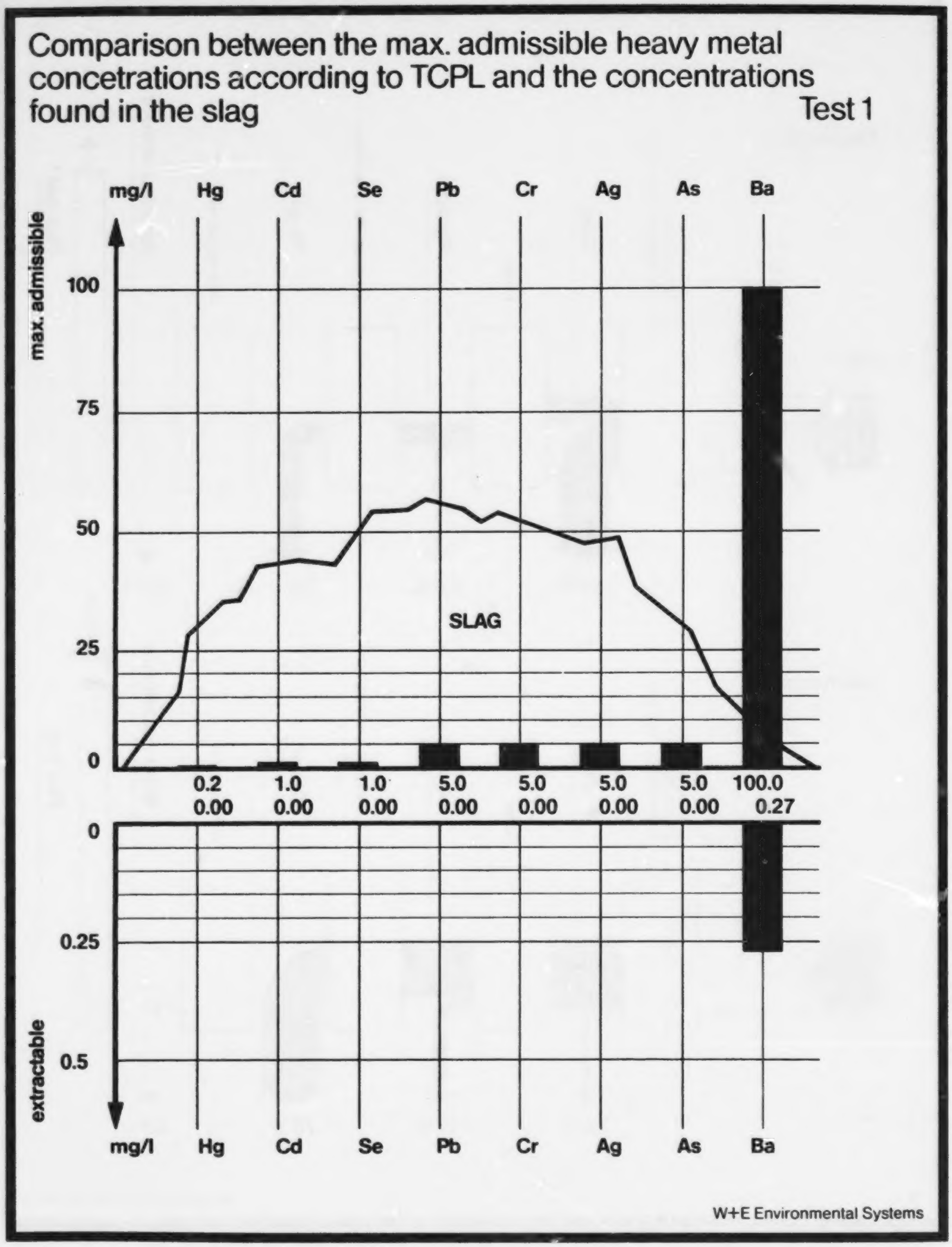

Cobalt (Co)
100%
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
0,3%
Flue gas
86%
3,9%
9,6%
0,1%
Chromium (Cr)
100%
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
0,4%
Flue gas
92%
2,5%
5,1%
0,1%

W+E Environmental Systems


Copper (Cu)
100 %
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
0,2 %
Flue gas
67 %
3,6 %
29 %
0,2 %
Cadmium (Cd)
100 %
Rotary kiln
Secondary combustion chamber
Slag
Boiler
Fly ash
Electrostatic precipitator
Fly ash
Wet scrubber
Scrubber effluent
Stack
0,3 %
Flue gas
3,2 %
18 %
78 %
0,1 %

W+E Environmental Systems

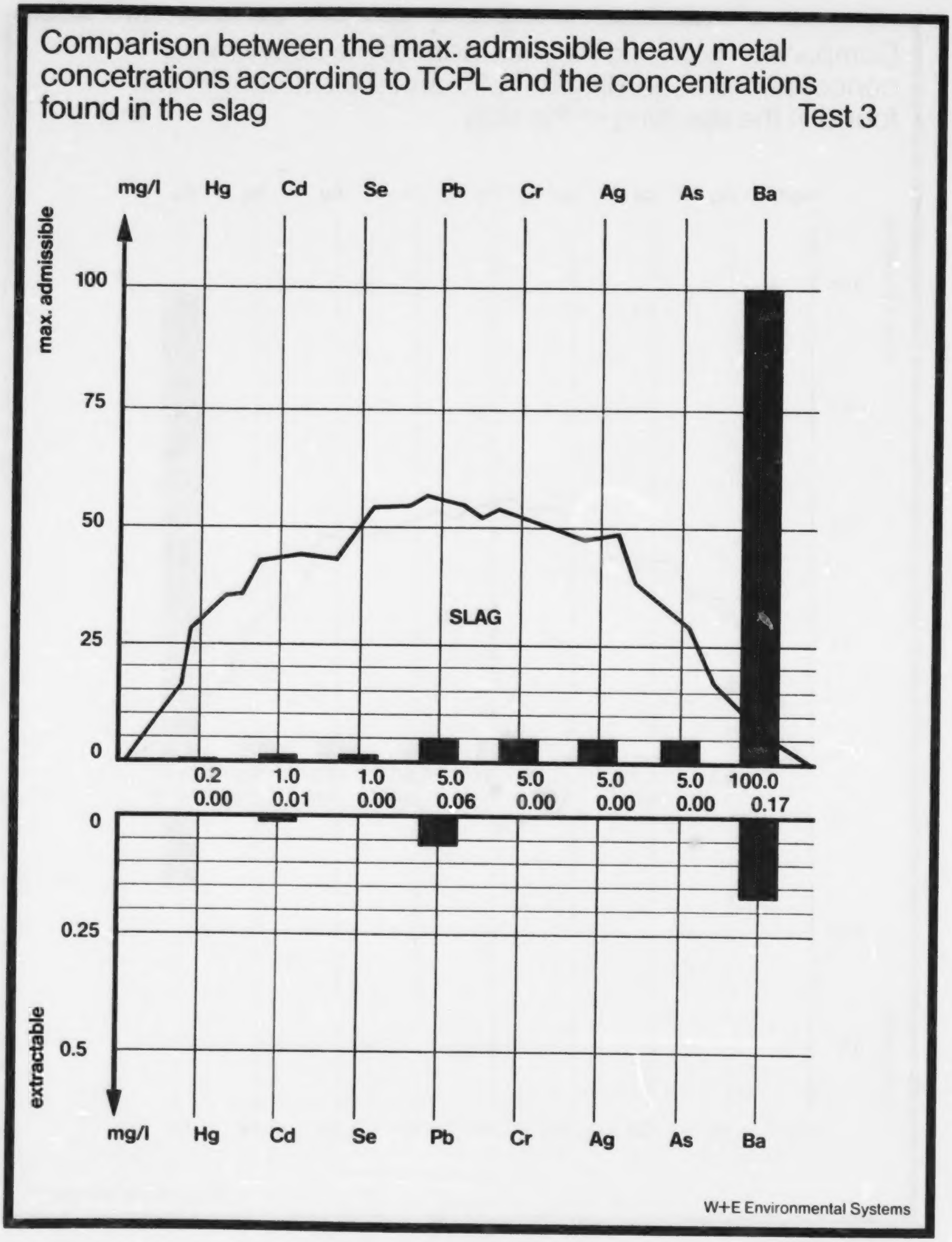
Fig. 6.1



Comparison between the max. admissible heavy metal concetrations according to TCPL and the concentrations found in the slag Test 1

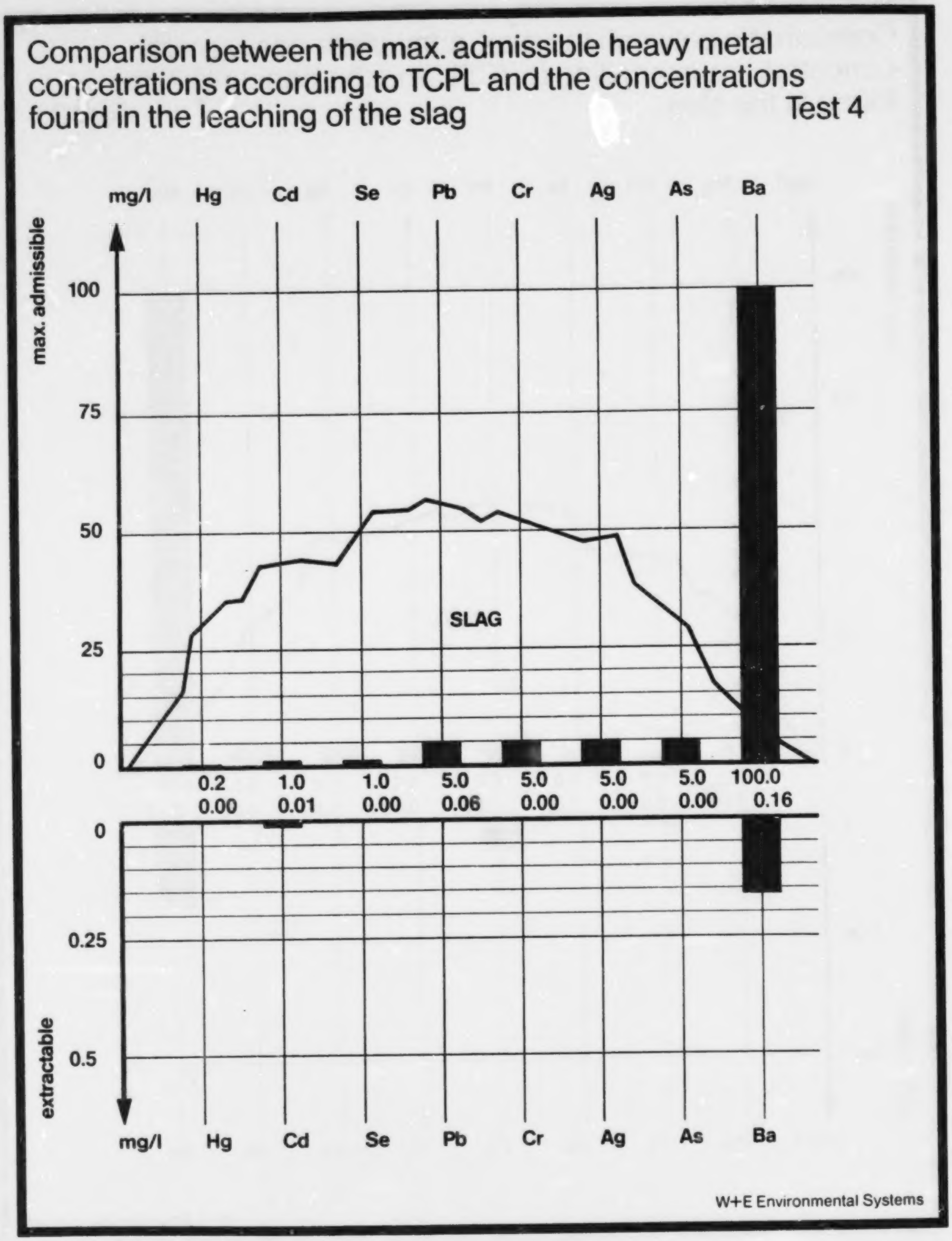
W+E Environmental Systems

Fig. 6.2



Comparison between the max. admissible heavy metal concetrations according to TCPL and the concentrations found in the slag Test 3

Fig. 6.3



Comparison between the max. admissible heavy metal concetrations according to TCPL and the concentrations found in the leaching of the slag Test 4

W+E Environmental Systems

TABLE 8 - EP-TOX ANALYTES AND MAXIMUM ALLOWABLE CONCENTRATION

ANALYTE	MAXIMUM CONCENTRATION mg/l
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.02
Lindane	0.4
Methoxychlor	10.0
Toxaphene	0.5
2, 4-D	10.0
2,4,5-TP (Silvex)	1.0

TABLE 9 - TCLP ANALYTES AND MAXIMUM ALLOWABLE CONCENTRATIONS

ANALYTE *	MAXIMUM CONCENTRATION mg/l
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0
Endrin	0.003
Lindane	0.06
Methoxychlor	1.4
Toxaphene	0.07
Heptachlor	0.001
a-Chlordane	0.03
r-Chlordane	0.03
2, 4-D	1.4
2,4,5-TP	0.1
Phenol	14.4
bis (2-Chloroethyl)ether	0.05
1,4-Dichlorobenzene	10.8
1,2-Dichlorobenzene	4.3
2-Methylphenol	10.0
4-Methylphenol	10.0
Hexachloroethane	4.3
Nitrobenzene	0.13
Hexachlorobutadiene	0.72
2,4,6-Trichlorophenol	0.30
2,4,5-Trichlorophenol	5.8
3-Methylphenol	10.0
Pyridine	5.0
2,3,4,6-Tetrachlorophenol	1.5
2,4-Dinitrotoluene	0.13
Hexachlorobenzene	0.13
Pentachlorophenol	3.6

* Volatile organic compounds were not analyzed.

Recycling of contaminated river and lake sediments demonstrated by the example of Neckar sludge

Dipl.-Ing. M. Nußbaumer, M.Sc. * and Dipl.-Ing. E. Beitinger °

Summary

The Neckar is an approximately 370 km long tributary of the Rhine, its confluence with the same being not far downstream from Heidelberg. The river was made navigable over a length of 202 km during the decades following the last World War, i.e. weirs with locks were constructed at some 20 km intervals along the river to regulate the water-level. Primarily fine-grained, suspended and sedimentary materials are deposited in the storage ponds and lead to the necessity of river dredging.

The purposes of the dredging are

- to keep the navigation lane open,
- to maintain the required river cross-section for flood control and
- to maintain water quality.

The dredged material has become contaminated by heavy metals due to the expansion of industry in the area, cadmium being the prime example. The sometimes high cadmium contamination precludes the use of the dredged materials for agricultural purposes. It was therefore initially proposed that the dredged sludge be dried and dumped at waste disposal sites. Since sites for waste disposal are rare and expensive to put into operation in the Federal Republic, economic means of recycling had to be sought.

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* Managing director, Ed. Züblin AG, Civil Engineering Contractors, Stuttgart, FRG

° Senior engineer, Ed. Züblin AG, Stuttgart, FRG

Toward this end one of the largest civil engineering contractors in the FRG, Ed. Züblin AG of Stuttgart, has developed a process whereby dredged material is converted into spherical, porous, lightweight aggregate for the production of masonry blocks and lightweight concrete.

The above-mentioned company has been awarded a contract to construct and operate a plant for the thermal treatment of 500,000 m^3 of sludge dredged out of the Neckar over a period of 10 years. In order to enable the thermal procedure involving temperatures of up to 1150 °C to be successfully put into service in an environment-friendly manner, a new concept for outlet-gas treatment had to be developed and tested.

Contaminated sediments

Dredged sludges from rivers and harbours can no longer be used for agricultural purposes because of their high level of contamination. The quantity of sludge dredged by the water and river navigation authorities to maintain navigation lanes is however considerable: in 1982 a total of 48 million cbm was removed from Federal waterways, of these 11 million cbm were from the Elbe and 12 million cbm were from the Rhine alone.

During the last two decades some 2 million cbm of sediments have accumilated on the bed of the Neckar between Plochingen and Heilbronn. Although extensive measures to improve effluent quality have reduced heavy metal pollution, the heavy metal content of the sediments in such that they cannot be used for agricultural purposes.

One cbm of Neckar sediment contains 800 l water and 550 kg solids. 5 % of the solids are debris of organic or anthropogenic origin such as woods, bicycles, refrigerators and rubble. The major part is, however, of mineral origin and has found its way into the river by way of natural erosion in the river's catchment area. The material from the clay and silt fractions up to 0.063 mm amounts to 40 % by weight of the sediment on average, while sand and gravel between 0.063 and 60 mm also make up 40 % by weight of the sediment. The composition varies, however, considerably.

High levels of pollutants accumulate in the fine-grained sediments. A number of investigations have demonstrated that a larger quantity of heavy metals accumulates in the fine-grained fraction of the dredged sludges than in the sand and gravel fractions. The sand and gravel fractions can therefore be disposed of relatively easily, while the fine-grained sludge presents a considerable problem.

Of the pollutants, heavy metals, heavy metal compounds, salts and all organic materials which enter a watercourse as a result of industrial production present a significant problem. The focal point of the investigations of the dredged Neckar sludge was, however, the retention of cadmium, which was detected in concentrations of up to 240 mg/kg (dry weight). The permissible concentration in soil used for agricultural purposes is 3 mg/kg (dry weight).

Up to ten years ago dredged Neckar sludge was used for agricultural purposes in large quantities. A layer of sludge up to 1 m in thickness was spread over existing fields. This soil has now had to be removed in part due to the high concentrations of heavy metals. Other procedures, such as drying in air, mechanical dewatering and hardening with alkaline binding agents, require waste disposal sites for end storage. On the Neckar, the dredged material was to be partially dewatered in three air-drying plants and subsequently transported to three remote single-purpose waste disposal sites. The adoption of this approach met with considerable resistance.

Procedure to recycle contaminated sediments

As a result of the above, it was decided to largely avoid dumping Neckar sludge. Instead it was proposed that spherical, porous, lightweight aggregate be produced from the sludge by way of adding expanding clay, the aggregate having characteristics similar to expanded clay and being capable of use as a substitute building material in order to reduce the import of expensive pumice-stone.

The procedure involves transporting the dredged sludge to a central treatment plant at which an intermediate storage facility has been installed to even out seasonal variations in dredging activity. The sludge is then partially dewatered in a screen belt press (mechanical process) and mixed with clay and additives.

The amount of clay and expanded clay additive amounts to between 15 % and 30 % by weight depending on the required strength and heat insulation properties of the final product. The mixture is subsequently made into pellets and then dried, burnt and cooled in the actual rotary kiln plant. The temperature of combustion may rise up to 1150 °C. Heat is extracted from the outlet-gas to be used elsewhere in the system, thus ensuring a high degree of heat reclamation.

Development for full-scale operation.

The procedure has been developed for full-scale operation with the support of the Bundesminister für Forschung und Technologie (Federal Minister for Research and Technology) and tested in two stages. The development work was based on the results of innumerable laboratory tests to find suitable mixtures for the differing sludge compositions, clay content etc., all of which have to ensure sufficiently good product characteristics.

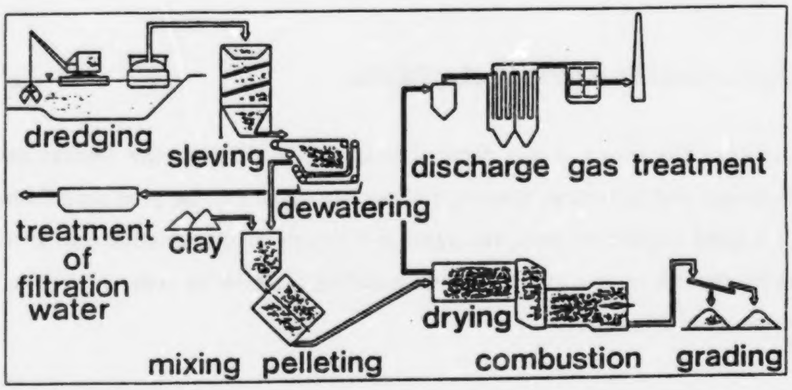

dredging
sleving
discharge gas treatment
dewatering
treatment of filtration water
clay
drying
mixing
pelleting
combustion
grading

Fig. 1. OPERATION SEQUENCE FOR RECYCLING SLUDGE

The main technical and scientific objective of the research and development programme was to prove that lightweight aggregate can be produced industrially from fine-grained river and lake sediments, that the aggregate's physical properties permit a wide range of applications and that the procedure can be operated economically. The production of the lightweight aggregate must be favourably priced, sure in operation, environment-friendly and adaptable to variations in raw material quality.

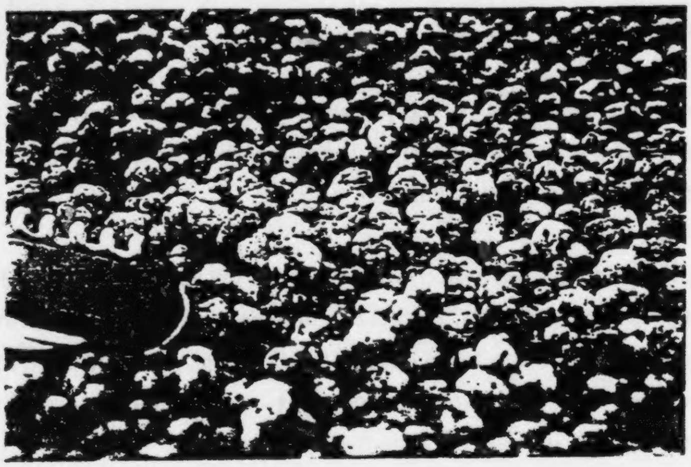


Fig. 2. Pellets of dried Neckar sludge and expanded clay.

Neckar sludge served as the "raw material", the sludge having been dredged out of the upstream area of locks and demonstrating a wide spectrum with respect to both its grain-size distribution and its contamination.

Pretreatment of the sludge

The sludge must be dried before it is burnt. The drying is firstly mechanical in screen belt presses and then, in pellet-form, in the kiln plant drier. In order to achieve as high a solids content as possible before the sludge is fed into the thermal drying plant, numerous tests were caried out with screen belt presses and flocculation agents.

Expanded Clay Production using Neckar Sediments

An industrially-used expanded clay production plant was modified and used to produce expanded clay from Neckar sediments in the first and second test phases.

The mixture-ratios which had been selected during laboratory tests were shown to be suitable in the first test phase. The measured outlet-gas values were used as initial values to design the outlet-gas treatment. The second test phase was spent optimizing and testing a pilot outlet-gas treatment plant.

The end product is a lightweight aggregate of various sizes (0 - 16 mm). The expanded clay can be used as a building material. It has a high compressive strength, excellent insulation properties and is easy to handle.

The expanded clay was tested with reference to the requirements set out in DIN 4226, Part 2, for lightweight aggregates. All the requirements were met. The heavy metal content lies in the same region as is to be found in other building materials such as pumice, brick, aerated concrete and conventional expanded clay. Numerous tests have proven that the expanded clay is a suitable building material for walls.

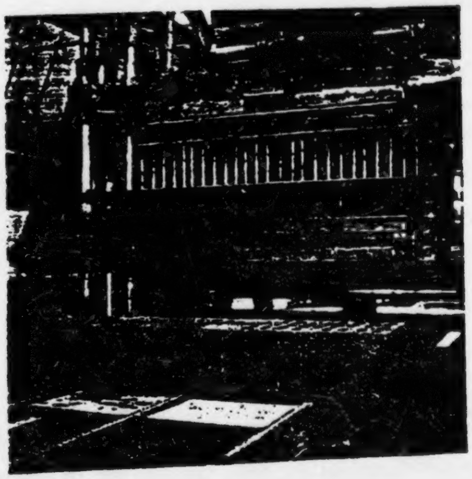


Fig. 3. Hollow masonry blocks leaving the press.

Hollow masonry and masonry blocks were produced in a cement works. These blocks also met all the requirements for outer and/or inner insulatory masonry blocks.

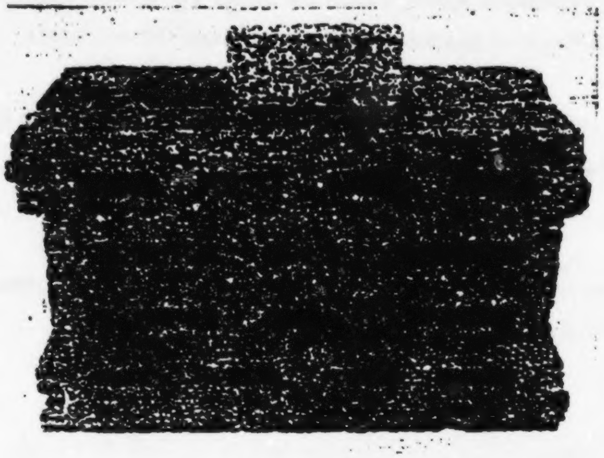


Fig. 4. Hollow masonry blocks made from Neckar sludge replace valuable raw materials and fulfil heat insulation requirements.

Outlet-Gas Treatment

There is no visible difference between the above-mentioned end product and expanded clay blocks. Waste, in this case contaminated river sludge, has been used to produce a first-class block and at the same time the use of valuable raw materials has been minimized.

Where have all the heavy metals gone? 100.000 m^3 of river sediments which are dredged out of the Neckar annually contain approximately 500 kg - 1000 kg cadmium. Cadmium has a boiling-point of 700 °C which is below the combustion temperature. The outlet-gas treatment has therefore to ensure that cadmium as well as other heavy metals and contaminants present in the outlet-gas are not emitted into the atmosphere.

The outlet-gas values were measured during the first test phase, analysed and interpreted. The areas concentrated on were heavy metals and the acidic gaseous components in the gas such as SO_x, NO_x, HF and HCl.

A treatment process capable of removing all these contaminants was not to be found so that a plant had to be designed by the contractors. The Landesanstalt für Umweltschutz in Karlsruhe (State Environmental Agency) took the outlet-gas measurements during the test phases on behalf of the Regierungspräsidium Stuttgart (State Government).

The outlet-gas treatment was designed in close cooperation with the Landesanstalt für Umweltschutz in Karlsruhe. The treatment process is in four stages.

Stage I

Cyclone and sleeve filters seperate out larger particles. These are returned to the production process at the mixing stage.

Stage II

A sleeve filter seperates out dust form the belt drier. This dust is also returned to the production process at the mixing stage. The outlet-gas then undergoes secondary combustion at temperatures of 800 - 900 °C and a residence time of more than one second. This waste heat is then recovered in a heat-exchanger which has an effectiveness of 75-80 %. The recovered heat is used to warm the belt drier.

Stage III

Dry absorption (lime dosage) with subsequent sleeve filter.

Stage IV

Double fines filter. The dust emitted into the atmosphere after these filters is less than 0.01 mg/Nm^3.

The outlet-gas system is hermetically sealed. Larger particles with a low contaminant concentration are seperated out of the outlet-gas in the cyclone. The sleeve filters then clean the air further and prevent the heat exchanger and the secondary combustion chamber from clogging up. Organic compounds are present in the gas released from the mixture whilst in the combustion kiln. These are turned into carbon dioxide (CO_2), water (H_2O) and hydrofluoric or hydrochloric acid (HF, HCl) in the secondary combustion chamber.

The acidic gaseous components present in the gas such as sulpher oxides (SO$_x$), hydrofluoric and hydrochloric acid (HF, HCl) react with lime (Ca(OH)$_2$) during the dry absorption to form solid, saline compounds which are retained in the sleeve filter.

The remaining heavy metal compounds are removed from the gas and are retained in the double fines filter. The dust collected in Stages III and IV is packed into drums and deposited at a waste disposal site.

Of the outlet-gas stream 2000 Nm^3/h was tested during pilot plant operation. Measurements were taken before, after and in between the various stages so that the treatment efficiency of the seperate stages and the treatment process as a whole could be ascertained.

All the outlet-gas values were well below those stipulated by the law at that time (TA-Luft 83) so that the values are still below those stipulated by the existing law (TA-Luft 86). In total 50,000 m^3 of Neckar sediments with an assumed cadmium content of 500 kg produce a dust emission of 1 - 3 kg and a yearly emission of less than 2 g cadmium into the atmosphere.

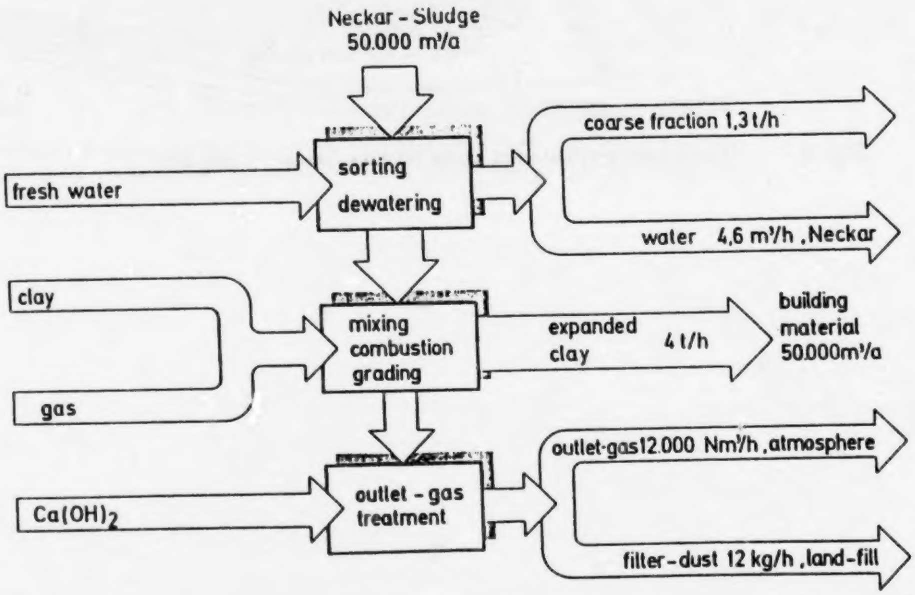

Neckar - Sludge
50.000 m³/a
fresh water
sorting
dewatering
coarse fraction 1,3 t/h
water 4,6 m³/h , Neckar
clay
gas
mixing
combustion
grading
expanded clay
4 t/h
building material 50.000m³/a
Ca(OH)2
outlet - gas treatment
outlet-gas 12.000 Nm³/h , atmosphere
filter-dust 12 kg/h , land-fill

Fig. 5. Expanded Clay Production using Neckar-Sludge - Throughput ZÜBLIN

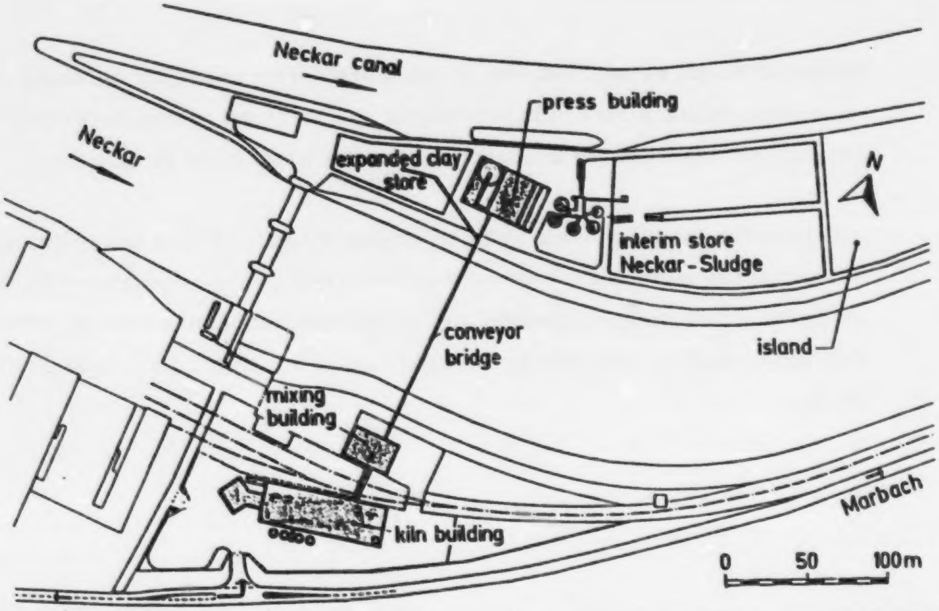

Neckar canal
press building
Neckar
expanded clay store
N
interim store Neckar-Sludge
conveyor bridge
island
mixing building
Marbach
kiln building
0
50
100m

Fig. 6. Expanded Clay Production using Neckar-Sludge - Site plan ZÜBLIN

FORUM
on
INNOVATIVE HAZARDOUS WASTE TREATMENT TECHNOLOGIES:
DOMESTIC AND INTERNATIONAL

Atlanta, Georgia
June 19, 20, and 21, 1989

OXYGEN ENHANCEMENT of HAZARDOUS WASTE INCINERATION WITH THE PYRETRON THERMAL DESTRUCTION SYSTEM

by Mark Zwecker, Fred Kuntz,
and Gregory Gitman
of AMERICAN COMBUSTION, INC.
NORCROSS, GEORGIA

ABSTRACT

A SITE program demonstration of the PYRETRON® Thermal Destruction System was conducted at the EPA's Combustion Research Facility (CRF). The PYRETRON TDS, developed by American Combustion, Inc. (ACI) of Norcross, Ga., was installed on the pilot scale rotary kiln incinerator. The demonstration tests were conducted using waste material from the Stringfellow Superfund site near Riverside, Ca. with a high heating value decanter tank tar sludge waste from coking operations. The test objectives were to evaluate ACI's claims that the PYRETRON TDS is capable of achieving:

- Control of transient discharges of POHCs and PICs during operating upset conditions;
- Higher waste feed rates than conventional incineration;
- Economic system operation.

The demonstration test results showed that ACI's PYRETRON TDS achieved the RCRA 99.99 percent POHC DRE at a waste feedrate which was 100% greater than the maximum rate achieved under conventional incineration. Measured particulate emissions from the PYRETRON testing were significantly less than the required 180 mg per dscm corrected to 7 percent oxygen.

The PYRETRON TDS was also tested at the maximum conventional system feedrate but with a 60% increased mass charge size. During these tests the PYRETRON system was capable of handling the increased charge mass without unacceptable levels of "puffs" generation. The concentration of POHCs in the ash residue was consistently below detection limits.

SITE Demonstration Test Program

American Combustion, Inc. was selected as one of the first participants in the EPA's Superfund Innovative Technology Evaluation (SITE) program. The SITE program aids in the commercialization of alternative and innovative hazwaste treatment technologies.

Within the SITE program, ACI performed a demonstration of the PYRETRON Thermal Destruction System (PTDS). The PTDS is an oxygen enhanced combustion system using ACI's patented technology designed for waste incinerators. The PTDS also incorporates a proprietary process control algorithm designed to anticipate, detect, and respond to prefailure conditions within the system.

The testing and evaluation of the PTDS took place at the EPA's Combustion Research Facility (CRF). The CRF is a fully permitted incinerator established by the EPA to conduct incineration testing and research. The testing occurred at the end of 1987 and beginning of 1988.

ACI, the EPA, and Accurex, the operating contractor of CRF, developed a test program to evaluate the PTDS versus a conventional air based incineration system. The test program objectives were:

1. Evaluate the PTDS' ability to reduce the magnitude and/or number of transient upsets ("puffs");

2. Achieve the RCRA 99.99% DRE at significantly higher feedrates than that attainable in the conventional system;

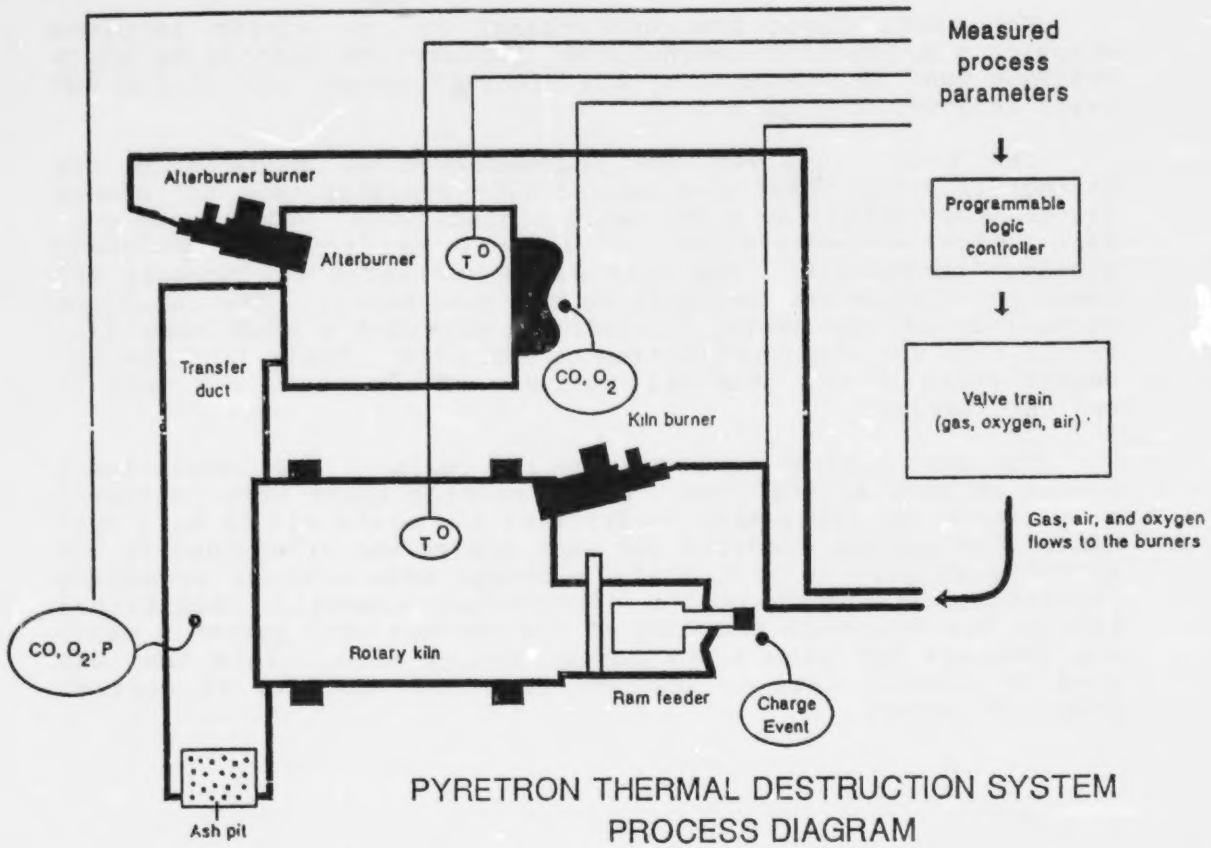
3. Improve the overall system economics compared to the conventional system.

For these tests the only change to the system involved removing the existing conventional burners and installing ACI's PYRETRON TDS. A schematic of the PYRETRON system used in the CRF tests is shown in Figure 1.

The tests involved the incineration of waste from the Stringfellow Superfund site spiked with decanter tank tar sludge (listed K087 waste) at a 2/3 ratio respectively. K087 waste contains high concentrations of several hazardous polynuclear aromatic components. The K087 waste was added to increase the level of volatile contaminants in the feed matrix. The resulting volatility of the waste, therefore, provided a much more difficult test for the capabilities of the PTDS. Table 1 of the Appendix contains the chemical analysis of the waste mix used in the CRF testing.

The test program included scoping tests of the conventional system as well as the PTDS. These scoping tests were performed to maximize the total mass feedrate of the waste mix in both systems. The maximum feedrate for each system was determined by the system's ability to incinerate a charge mass without exceeding regulatory CO limits in the afterburner exhaust. Additional testing was done with the PTDS at the conventional system's maximum feedrate but with a 60% larger charge mass. This test was used to provide data to confirm the PTDS' ability to control transient upsets.

FIGURE 1 - SCHEMATIC OF THE PYRETRON THERMAL DESTRUCTION SYSTEM TESTED AT CRF


Measured process parameters
Programmable logic controller
Valve train (gas, oxygen, air)
Gas, air, and oxygen flows to the burners
Afterburner burner
Afterburner
T°
CO, O2
Kiln burner
Transfer duct
T°
CO, O2, P
Rotary kiln
Ram feeder
Charge Event
Ash pit

PYRETRON THERMAL DESTRUCTION SYSTEM PROCESS DIAGRAM

Test Results

The optimum mass feedrate of the conventional system was established at 105 pounds per hour. This rate was accomplished by feeding mass charges of 21 pounds every 12 minutes. Data obtained from the conventional system during this test is contained in Figure 2.

Figure 3 shows data from the conventional system operating at a charge mass and interval slightly above the optimum. The operating data at this feedrate shows many failures due to the depletion of available oxygen in the kiln atmosphere. As a result, the system experienced flame failures, system pressure excursions, and excessive process temperatures commonly associated with the development of "puffs." The conventional system was incapable at the increased feedrate of simultaneously maintaining sufficient excess oxygen and reducing auxiliary fuel input to control the upset.

The corresponding optimum mass feedrate for the PTDS was established at 210 pounds per hour. This rate was accomplished by feeding mass charges of 21 pounds every 6 minutes. Data for the PTDS during this test is shown in Figure 4. The feedrate demonstrated by the PTDS is twice the optimum feedrate of the conventional system.

Stack test results showed that the PTDS was able to achieve greater than 99.99% DRE at the increased feedrate. Stack samples taken during the optimum feedrate test run did not detect any POHC. There was also no detection of POHC within the ash residue or scrubber effluent from this test. The PTDS also operated well within the regulatory limit of 180 mg per dry scm for particulate emissions. Table 2 located in the Appendix lists the results of the stack particulate testing.

Figure 5 shows the data for the PYRETRON system at a charge mass of 34 pounds and a charge interval of 19.5 minutes. This charge mass represents a 60% increase over the optimum mass which the conventional system could handle. Under these operating conditions, the PTDS provided enough oxygen to the system to control CO discharge from the kiln. As a result, the afterburner system was not overloaded at these conditions and failures were prevented.

FIGURE 2

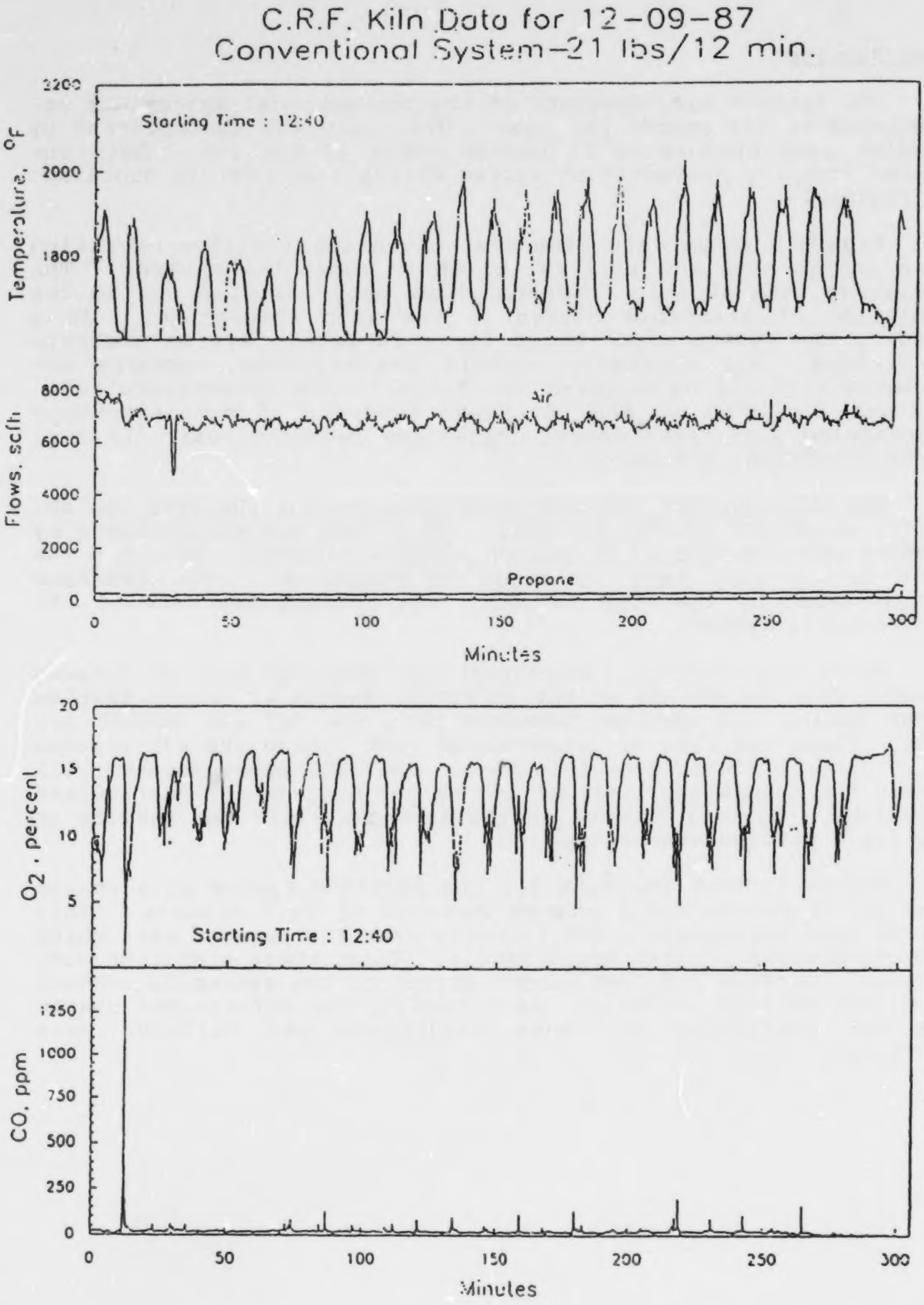
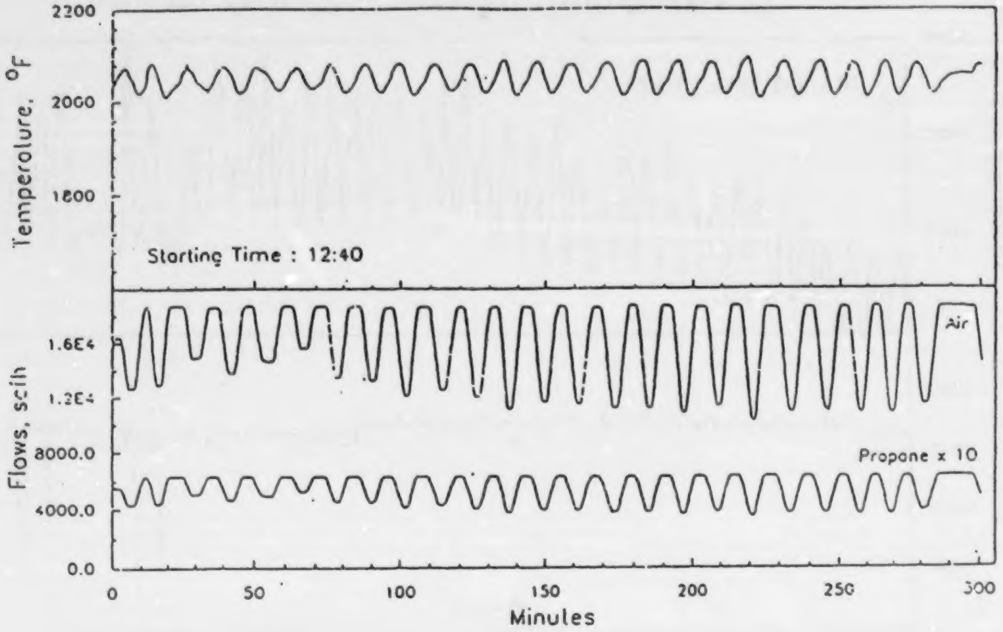
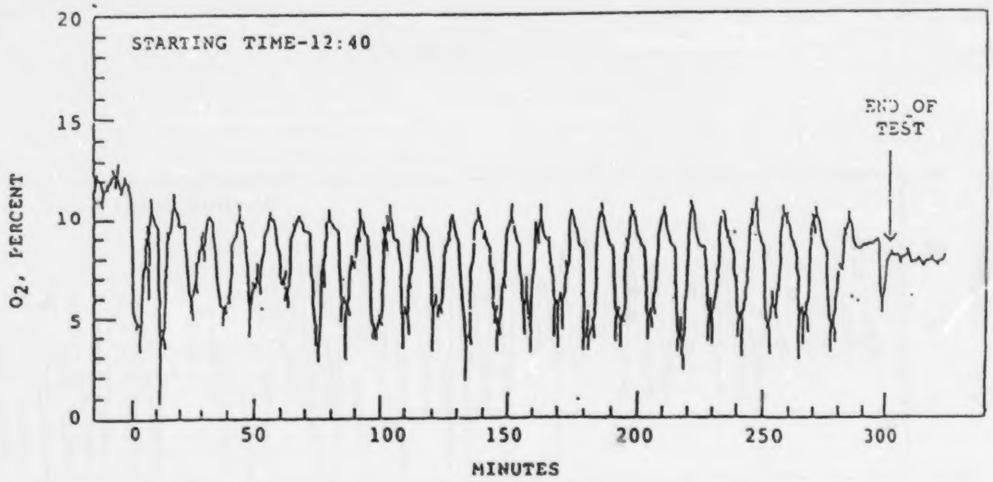
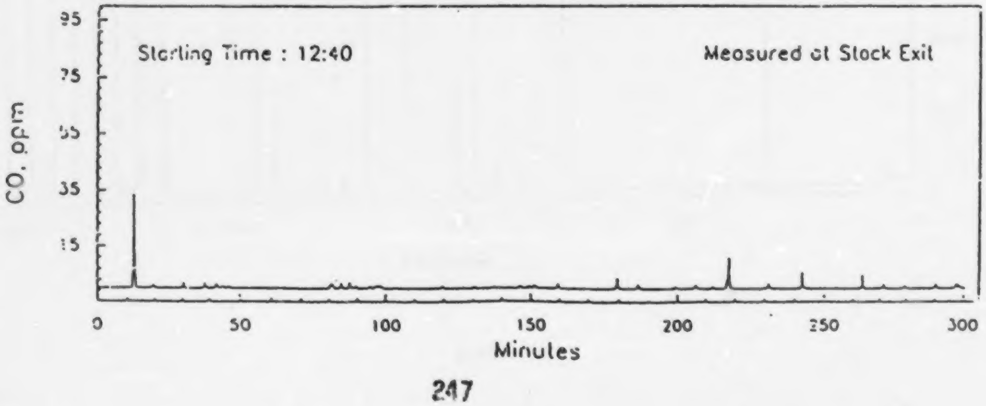

C.R.F. Kiln Data for 12-09-87
Conventional System-21 lbs/12 min.
Starting Time : 12:40
Temperature, °F
2200
2000
1800
Air
Flows, scfh
8000
6000
4000
2000
0
Propane
0
50
100
150
200
250
300
Minutes
20
15
10
5
O2, percent
Starting Time : 12:40
CO, ppm
1250
1000
750
500
250
0
0
50
100
150
200
250
300
Minutes

FIGURE 2 (CONTINUED)



C.R.F. Afterburner Data for 12-09-87
Conventional System-21 lbs/12 min.





C.R.F. Stack Data for 12-09-87
Conventional System-21 lbs/12 min.

FIGURE 3

C.R.F. Kiln Data for 12-08-87
Conventional System – 24 lbs/10 min.

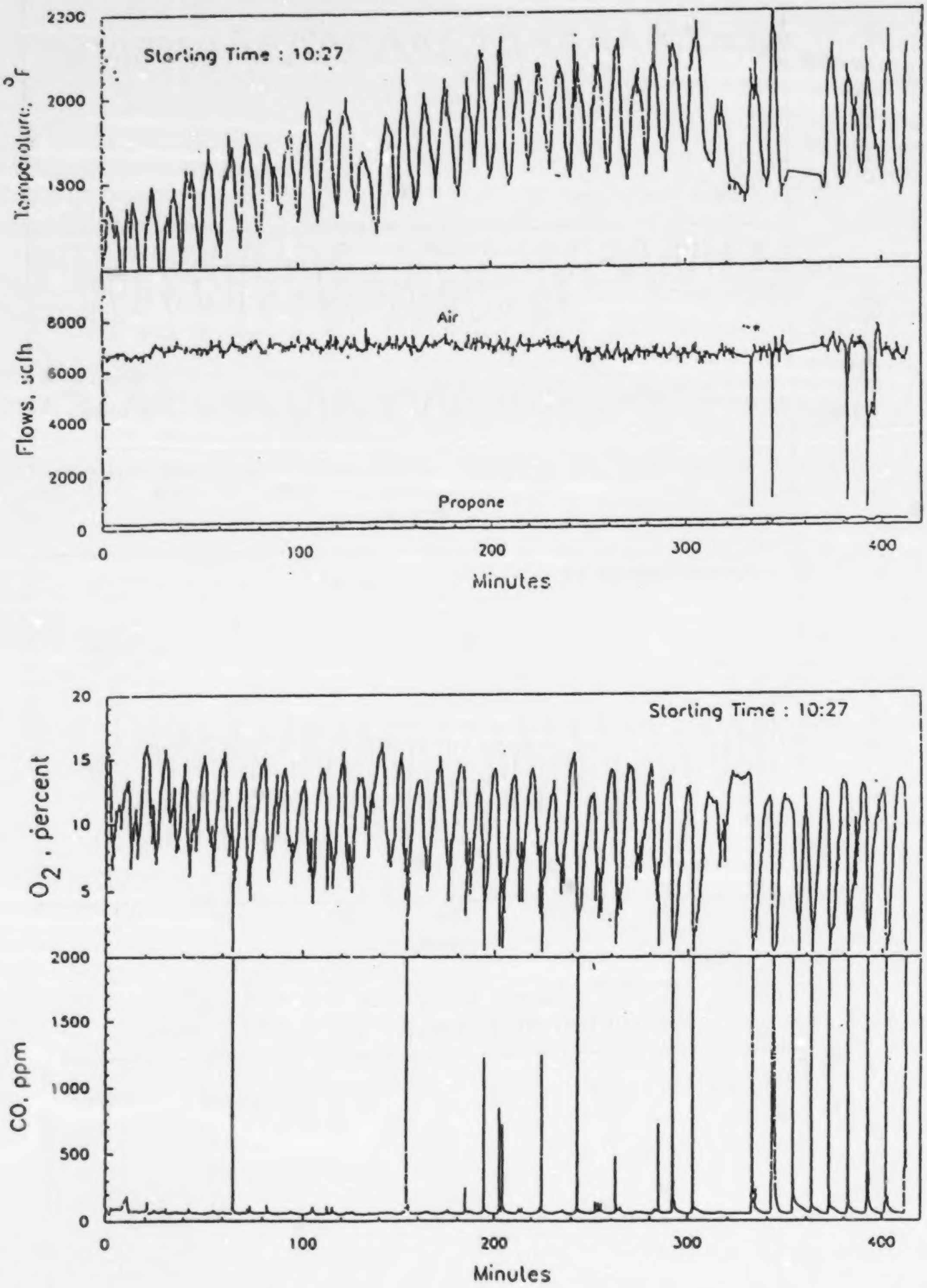
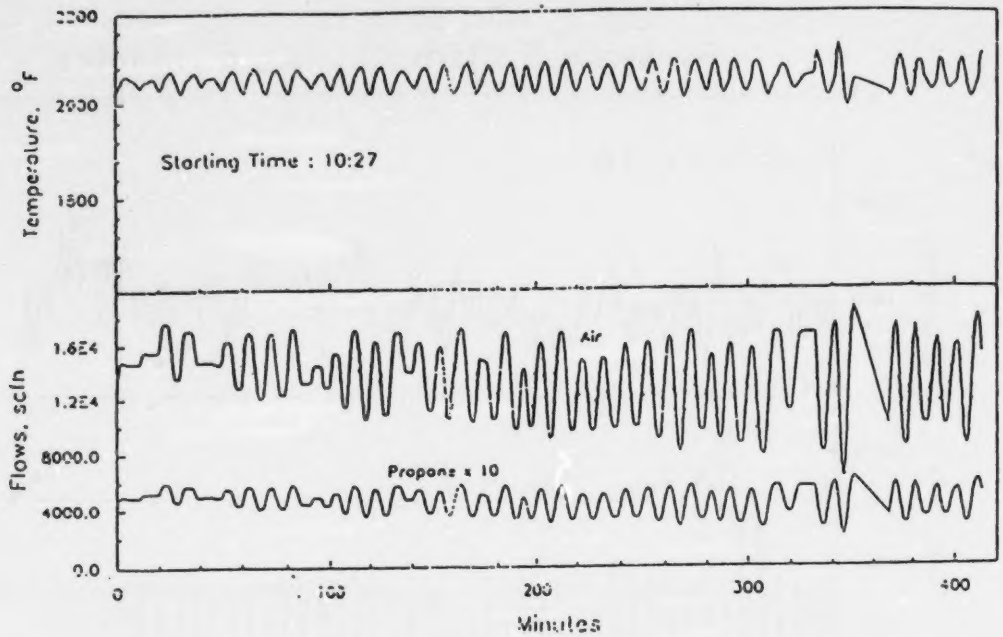
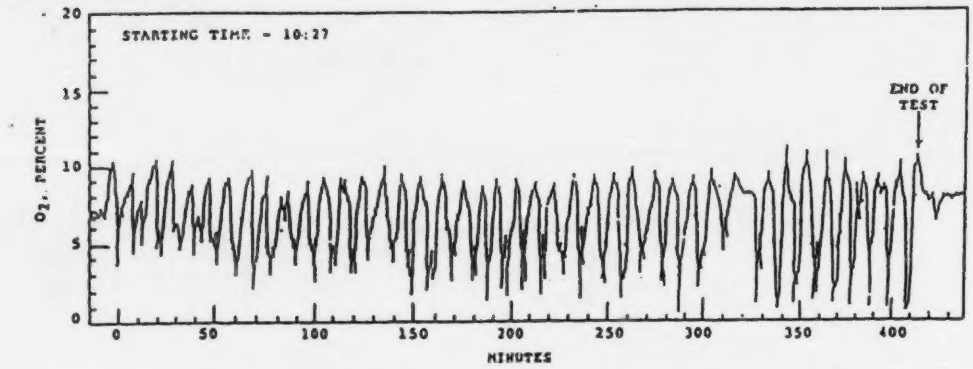


FIGURE 3 (CONTINUED)

C.R.F. Afterburner Data for 12-08-87
Conventional System-- 24 lbs/10 min.





C.R.F. Stack Data for 12-08-87
Conventional System--24 lbs/10 min.

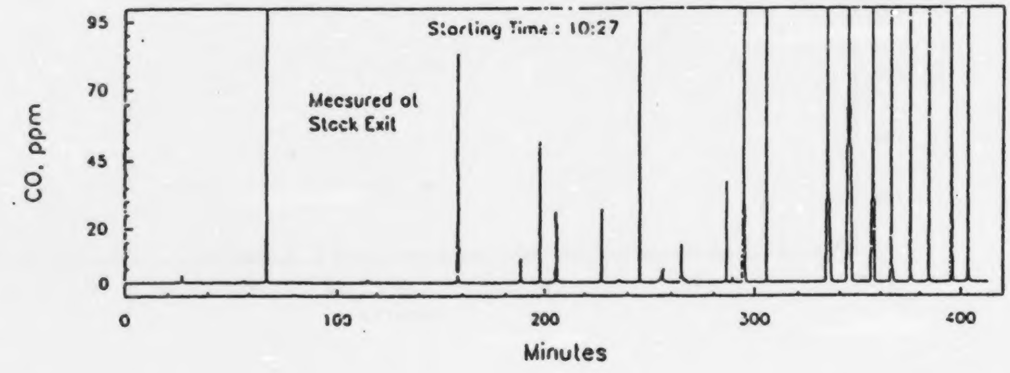


FIGURE 4

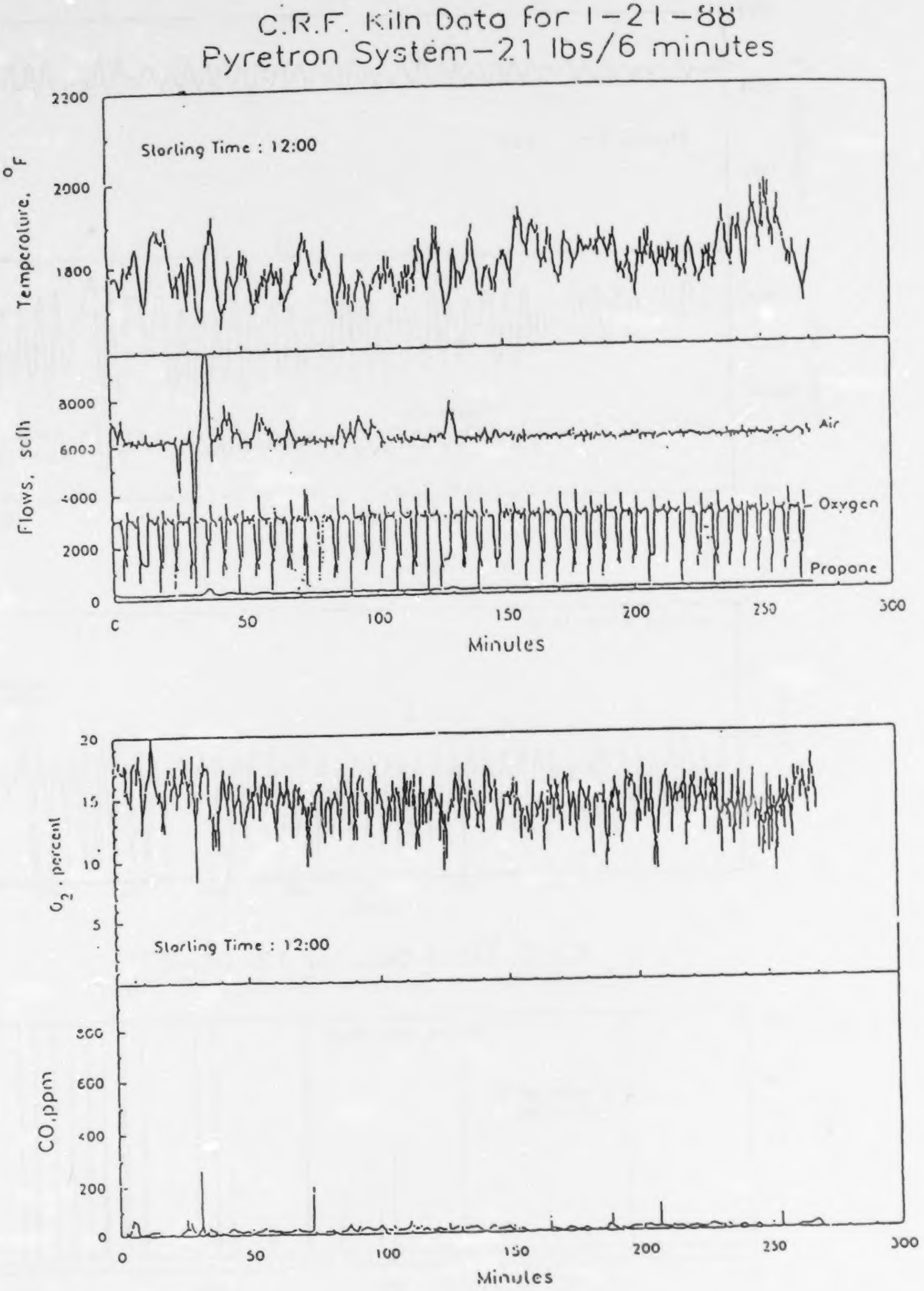
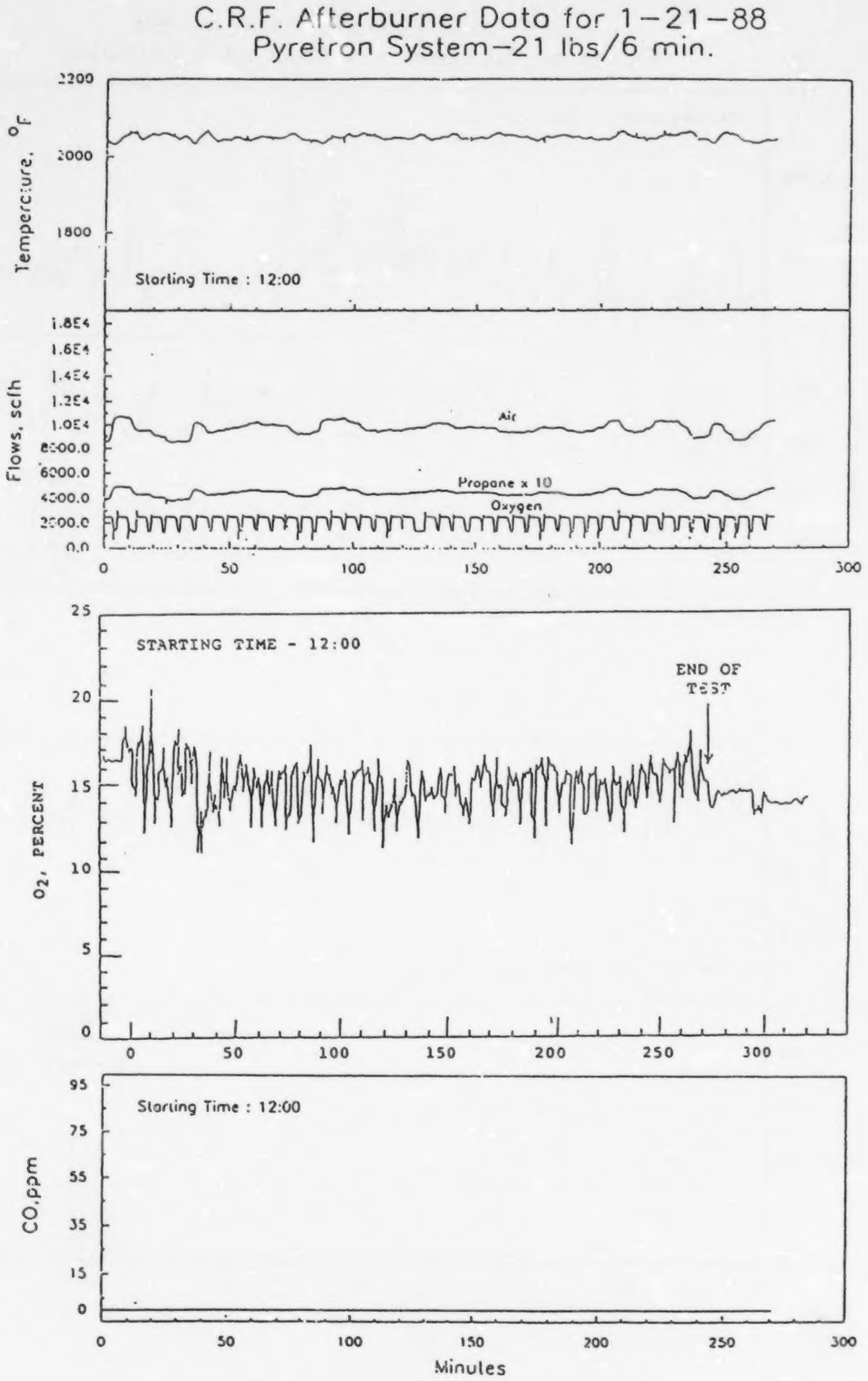

C.R.F. Kiln Data for 1-21-88
Pyretron System-21 lbs/6 minutes
Starting Time : 12:00
Temperature, °F
2200
2000
1800
Flows, scfh
8000
6000
4000
2000
0
Air
Oxygen
Propane
0
50
100
150
200
250
300
Minutes
O_2, percent
20
15
10
5
Starting Time : 12:00
CO, ppm
800
600
400
200
0
0
50
100
150
200
250
300
Minutes

FIGURE 4 (CONTINUED)



C.R.F. Afterburner Data for 1-21-88
Pyretron System-21 lbs/6 min.

FIGURE 5

C.R.F. Kiln Data for 1-14-88
Pyretron System--34 lbs/19.5 minutes

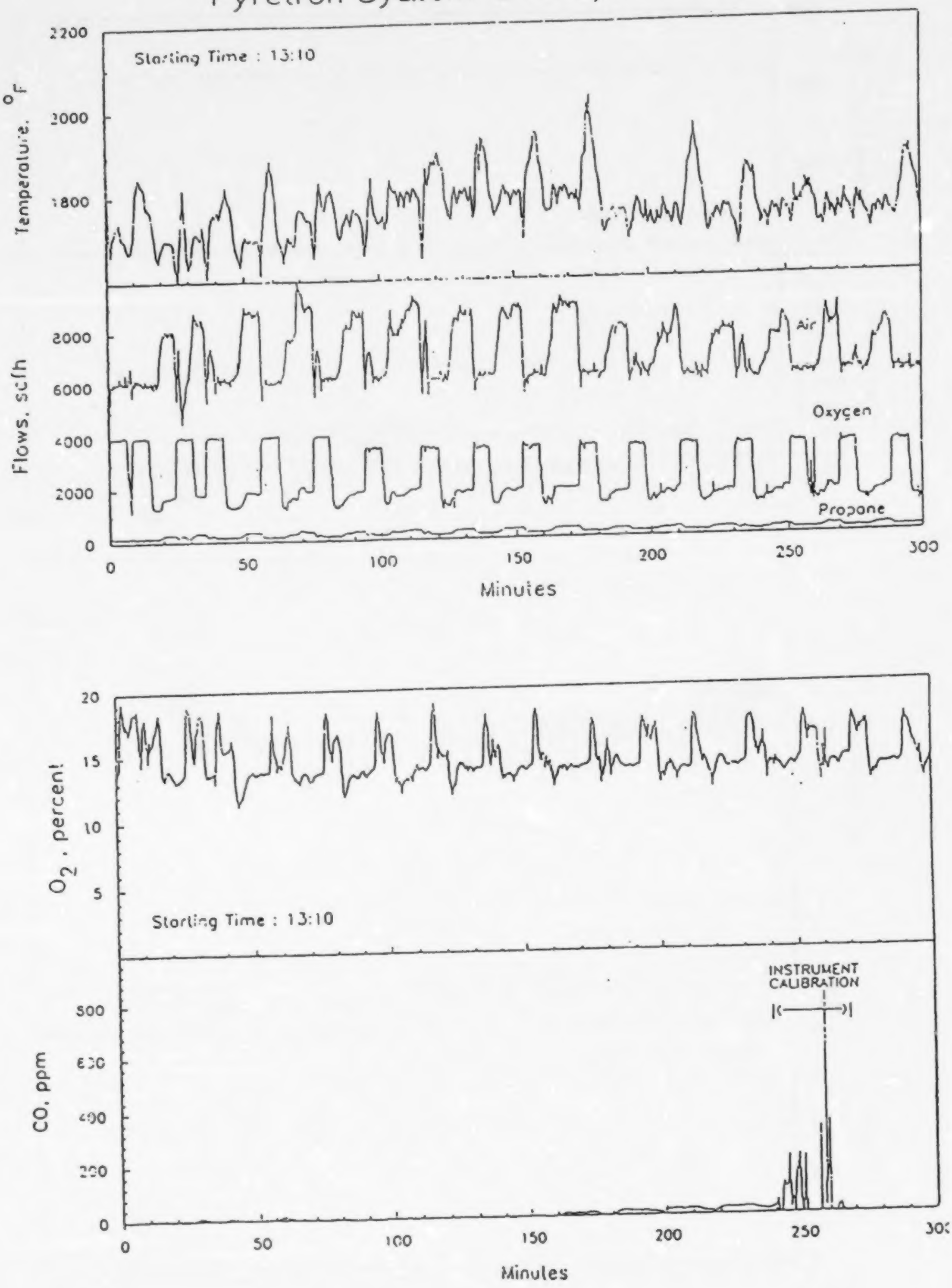
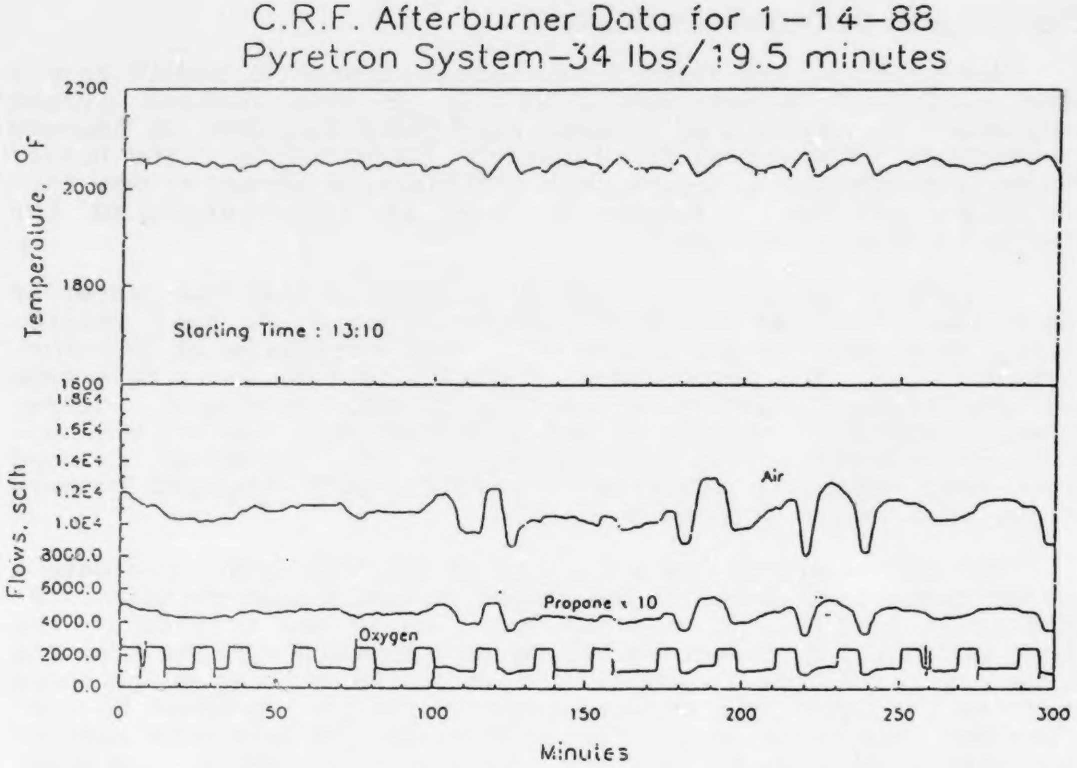
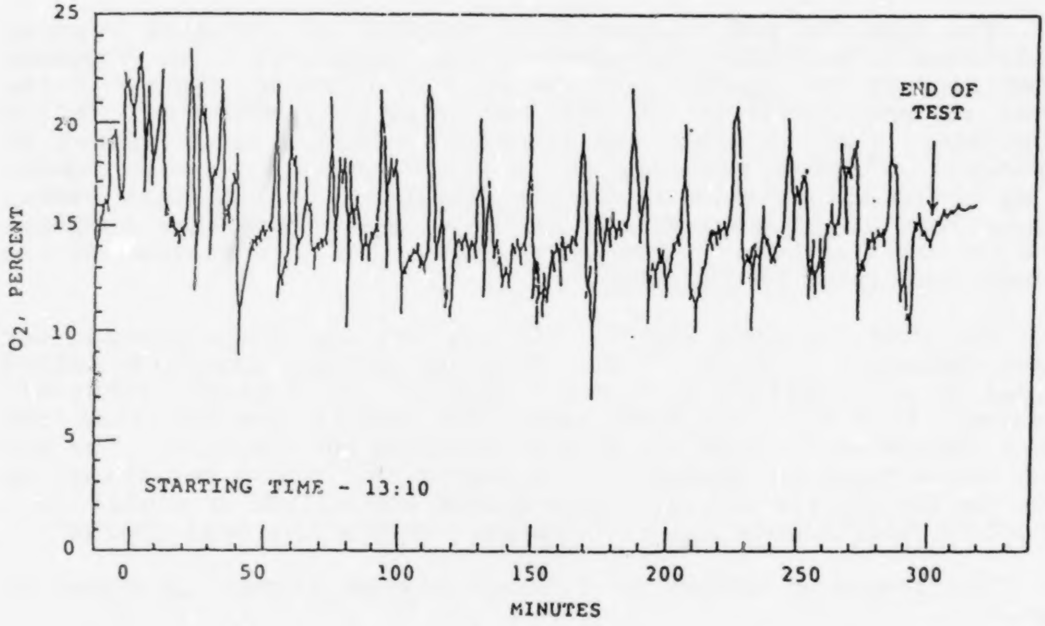


FIGURE 5 (CONTINUED)



C.R.F. Afterburner Data for 1-14-88
Pyretron System-34 lbs/19.5 minutes



PTDS Process Improvement Summary

The process improvements provided by the PTDS result from a more efficient burner design and a process control system programmed to adjust the process parameters required to improve destruction efficiencies for hazardous constituents. The burner design incorporates a second more concentrated oxygen stream into the flame pattern. Figure 6 shows an illustration of the PYRETRON burner flame pattern.

Oxygen is fed at sub-stoichiometric rates into the center of the flame. Even at sub-stoichiometric rates the heat release within this core is sufficient to cause pyrolysis of the surrounding fuel. The pyrolysis products of combustion in this zone are more highly radiative at the temperatures developed. Consequently, energy is rapidly transferred from this zone to the surrounding atmosphere. Flame temperatures are, therefore, reduced from those typically achieved by traditionally designed burners at the same oxygen enrichment level.

Air is fed around the periphery of the fuel zone to create a cooler combustion zone at the edges of the flame pattern. At this point the fuel is burning from inside and outside of the flame pattern. By directing the various process streams from the burner, a third zone is created in which the combustion products from the pyrolytic and excess oxygen zones are combined to complete the combustion of the fuel. This results in a high combustion efficiency even at very low stoichiometric ratios. In addition, highly reactive excess oxygen exits the stable flame envelope at elevated temperatures.

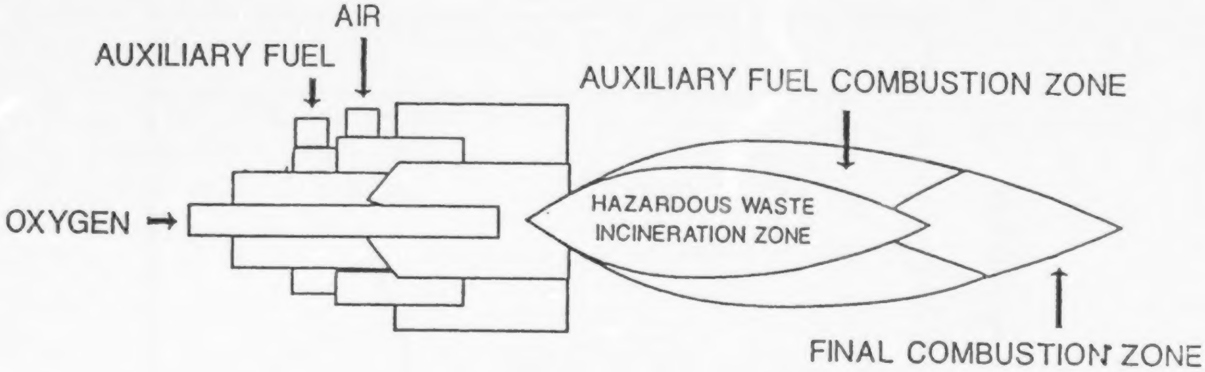
PTDS Control

The PTDS is preprogrammed to respond to changing process conditions to maintain high destruction capability. The response capability of the system involves an instantaneous change in the level of participation of the two oxidizing streams. ACI's proprietary control algorithm provides a series of responses to various instrument readings to maintain optimum process conditions. Conditions such as system pressure, insufficient excess oxygen levels, high CO concentrations, low afterburner temperature, as well as other potential "upsets" can be contained by the changes initiated by the PTDS.

The PTDS designed for the CRF testing was preprogrammed for three response actions. One response action involved adding oxygen in anticipation of a batch charge. At a preset interval, a signal from the ram feed mechanism alerts the PLC that the waste charge would soon be introduced into the furnace. The PLC then automatically responded by changing the oxygen participation rate to change the furnace atmosphere to include a significant amount of hot, highly reactive oxygen before the mass charge.

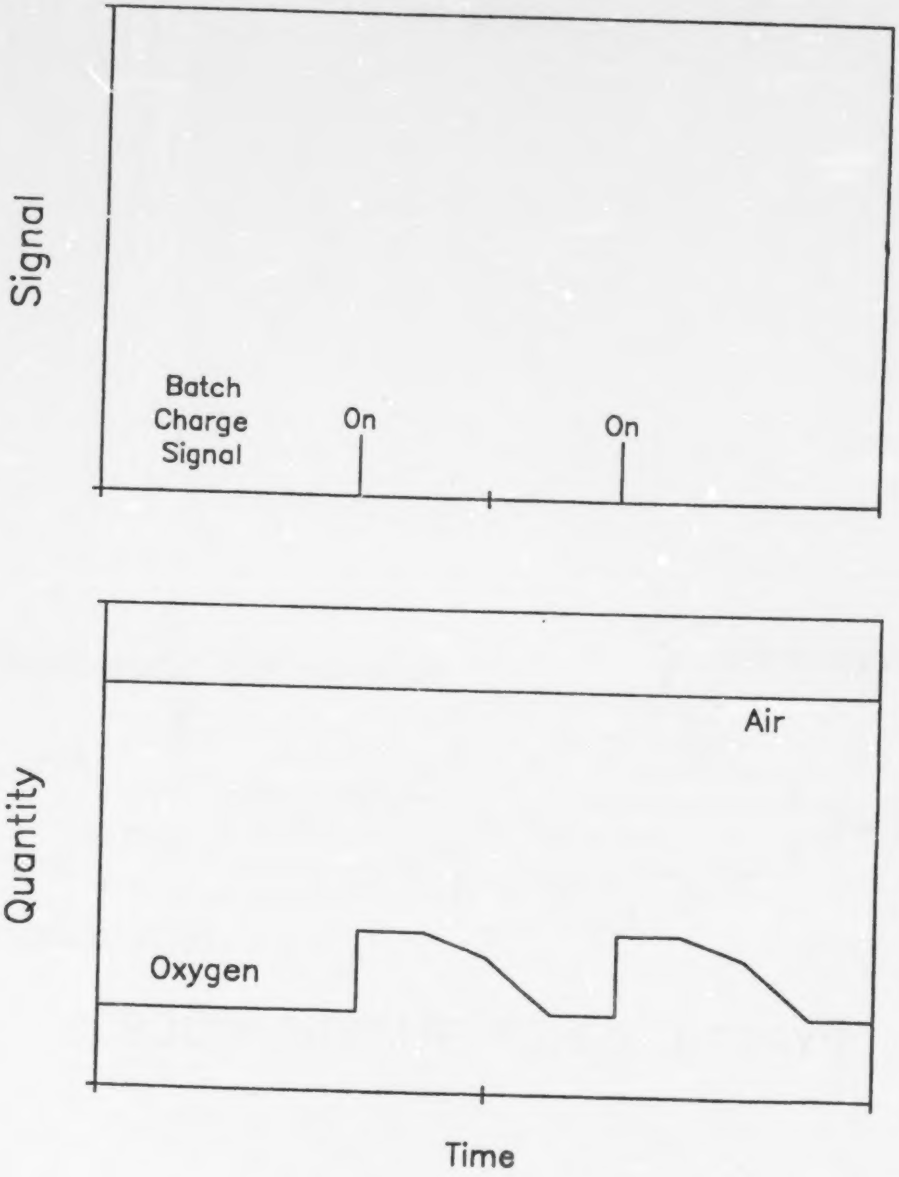
The response action to a batch charge signal is shown in Figure 7.

FIGURE 6


AIR
AUXILIARY FUEL
AUXILIARY FUEL COMBUSTION ZONE
OXYGEN →
HAZARDOUS WASTE INCINERATION ZONE
FINAL COMBUSTION ZONE

PYRETRON INCINERATION PROCESS

FIGURE 7



PYRETRON
Oxygen Based
Control Response
to a
Batch Charge Signal

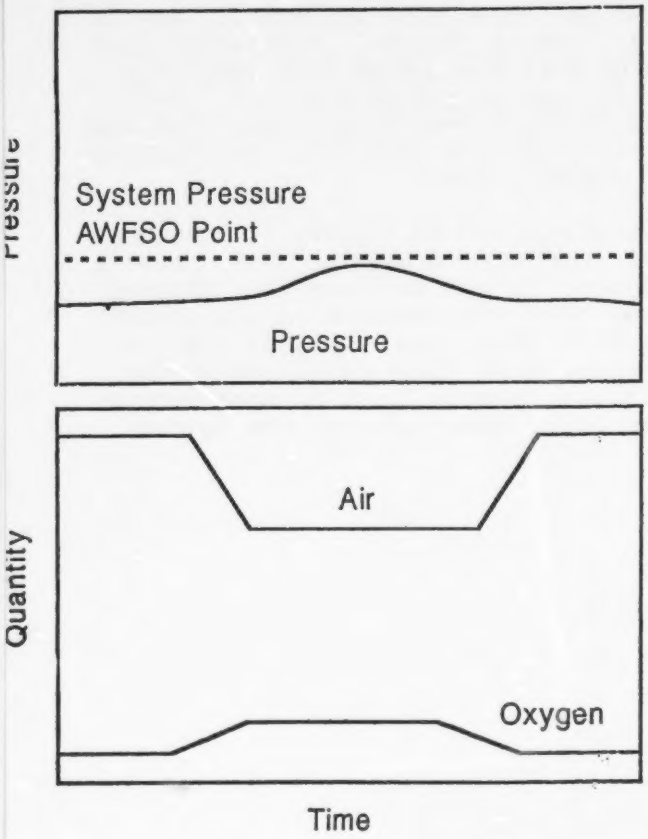
As a result of the PTDS' response, the potential for depleting oxygen at the initiation of the charge into the furnace was reduced. Therefore, the reaction of the volatiles in the batch charge was completed thus preventing the generation of much of the "puffs" that occurred in the conventional system. A water quench spray, controlled by the PLC, was used to dissipate excess heat released from the charge.

Another response action programmed into the PTDS is a response to system pressure excursions. This response, represented in Figure 8, permits the quantity of oxygen fed into the system to be maintained while the total gas volume is reduced.

By changing the oxygen participation rate, the volume of inerts fed into the system is reduced. As a result, the total gas volume does not exceed the maximum that the system can handle and fugitive emissions from the kiln seals are prevented. This response is also useful for systems which must maintain a minimum gas residence time. The response sequence can also be used to modulate low afterburner process temperatures.

The third response action, represented in Figure 9, involves a response to kiln exhaust gas analyzer signals that show a depletion of oxygen or an increase in CO exiting the primary chamber. When the analyzer showed that adjustments in the excess oxygen amount were required, the PTDS would again adjust the participation rate to prevent a failure mode from occurring. This response action is also useful for responding to a furnace oxygen deficiency or an excessive combustibles feed rate to the system.

FIGURE 8



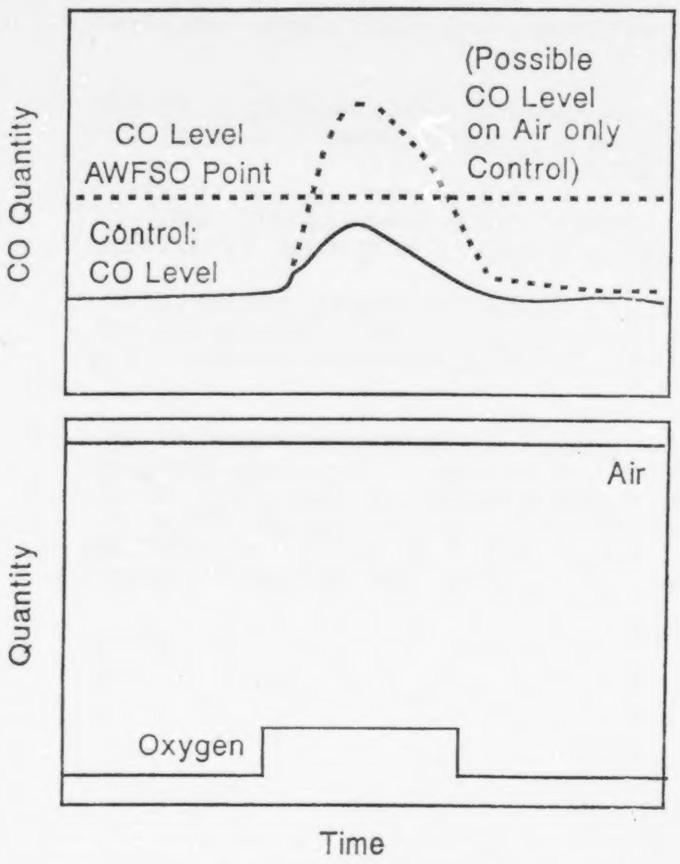
PTDS
Oxygen Based
Control Response
to
System Pressure

Also:

Low Gas Residence Time

Low Afterburner Process Temperature

FIGURE 9



PTDS
Oxygen Based
Control Response
to
Carbon Monoxide

Also:

Deficient Oxygen

Excessive Combustibles
Feed Rate

Conclusions

The EPA's Site program tests showed that the PTDS is capable of improving the environmental and economic performance of a conventional incineration system. The PYRETRON system accomplishes these improvements by a combination of innovative burner design and dynamic process control. Specifically, the EPA tests demonstrated that ACI's PYRETRON technology will:

1. Provide increased waste throughput capability by controlling "puffs" and improving DRE;
2. Only require a modification to the existing incinerator's combustion and combustion control equipment to achieve the PYRETRON technology improvements;
3. Achieve destruction efficiencies well above required levels;
4. Eliminate transient releases of POHCs and PICs to the environment by the system's preprogrammed Transient Upset Control response action;
5. Handle as much as a 60% increased batch load of volatile wastes without increasing hazardous emissions;

The PTDS is applicable to any waste treatment incinerator, including medical waste, which requires efficient control for environmental compliance. The PTDS is being marketed commercially by American Combustion, Inc.

American Combustion, Inc. has over ninety commercial applications which use the PYRETRON technology. These applications include electric arc furnaces, copper smelting furnaces, glass tanks, ladle heaters, and lead and aluminum refining furnaces. All of these applications use ACI's PYRETRON combustion systems as well as various aspects of ACI's patented dynamic control technology.

APPENDIX

TABLE 1 - CHEMICAL ANALYSIS OF WASTE FEED MIX USED IN PYRETRON TDS DEMONSTRATION TESTS

Component	Concentration, ppm
Naphthalene ($C_{10}H_8$)	49,772
Phenanthrene ($(C_6H_4CH)_2$)	22,569
Acenaphthalene ($C_{12}H_8$)	11,722
Fluoranthene ($C_{16}H_{10}$)	11,529
Pyrene ($C_{16}H_{10}$)	11,036
Anthracene ($(C_6H_4CH)_2$)	6,764
Fluorene ($C_6H_4\ CH_2\ C_6H_4$)	6,397
Dibenzofurane ($(C_6H_4)_2O$)	3,926
2-Methylnaphthalene ($C_{10}H_7\ CH_3$)	3,457
Miscellaneous PolyNuclear Aromatics	5,017
Miscellaneous Unknowns	1,031

TABLE 2 - PARTICULATE EMISSIONS DATA

Test	System	Particulate Concentration mg/dscm[a,b]	Particulate Concentration mg/dscm[c]
1	Conventional	8	4
2	Conventional	9	4
3	Conventional	47	28
4	Conventional	29	19
5	PYRETRON TDS	28	24
6	PYRETRON TDS	10	7
7	PYRETRON TDS	28	17
8	PYRETRON TDS	39	20

[a] Corrected to 7% oxygen for the air-only tests.

[b] PYRETRON tests were corrected to 7% oxygen considering the effect of oxygen enrichment.

[c] Uncorrected

Process Description and Initial Test Results with the Plasma Centrifugal Reactor

BY

R.C. Eschenbach, R.A. Hill & J.W. Sears

RETECH, INC UKIAH, CA

Forum on Innovative Hazardous Waste Treatment Technologies: Domestic and International

June 19-22 1989

Atlanta, GA

TITLE: PROCESS DESCRIPTION AND INITIAL TEST RESULTS WITH THE PLASMA CENTRIFUGAL REACTOR

AUTHORS: R. C. Eschenbach, R. A. Hill, and J. W. Sears, Retech,Inc. Ukiah, California

INTRODUCTION:

During the last few years Retech, Inc. has developed the Plasma Centrifugal Reactor (PCR) to stabilize solid waste material while decomposing any toxic hydrocarbons into relatively innocuous, simple molecules. The PCR uses heat from an arc to melt and vitrify solid components, thereby accomplishing the decomposition and stabilization of the waste. Plasmas can produce temperatures in excess of 10,000°C although the expected temperature to be produced in the molten glass will be about 1600°C.

The development of this furnace has been achieved through a three phase program. The first phase was directed at reducing the volume of radioactive mixed wastes. Initial tests were performed at Ukiah in Retech's 100 kW lab-scale plasma furnace, followed by demonstrations on surrogate materials in a titanium production furnace located at Oregon Metallurgical Corporation, Albany, Oregon. In phase two of this program a quarter-scale PCR was designed, built and tested at our Ukiah facility. During this phase the first patent covering the plasma centrifugal furnace was issued (U.S. Patent # 4,770,109). The final phase of this program will be to evaluate the performance of a full size furnace. Preliminary tests were performed in Ukiah (March-May 1989), while further tests will be run by the U.S. Department of Energy (D.O.E.) at their Magnetohydrodynamics facility in Butte, Montana, as part of the EPA's Superfund Innovative Technology Evaluation (SITE) program (summer 1989).

PHASE I (1985-1986)

The initial tests, conducted with a transferred-arc plasma on materials (metals, glass, rubber, plastics, filter elements, etc.) like those which get radioactively contaminated, demonstrated the effectiveness of volume reduction. The first tests were made in our lab-scale furnace by melting down pint cans filled with plastic gloves, rubber, ceramics and chunks of metal. Scale-up tests with an argon arc at about 1500 amperes and 130 volts were conducted on 4 liter steel cans stuffed with simulated waste. The resulting volume reduction was found to be a factor of 20 with the corresponding weight reduction at a factor of 1.8.(1) Problems with arc stability were encountered; contributing factors were vision problems caused by sooting shortly after each can was added and limited power supply voltage. It was concluded that the addition of oxygen or air as an oxidant in the plasma gas would be desirable in order to convert hydrocarbons to carbon dioxide and water instead of soot, carbon monoxide and hydrogen.

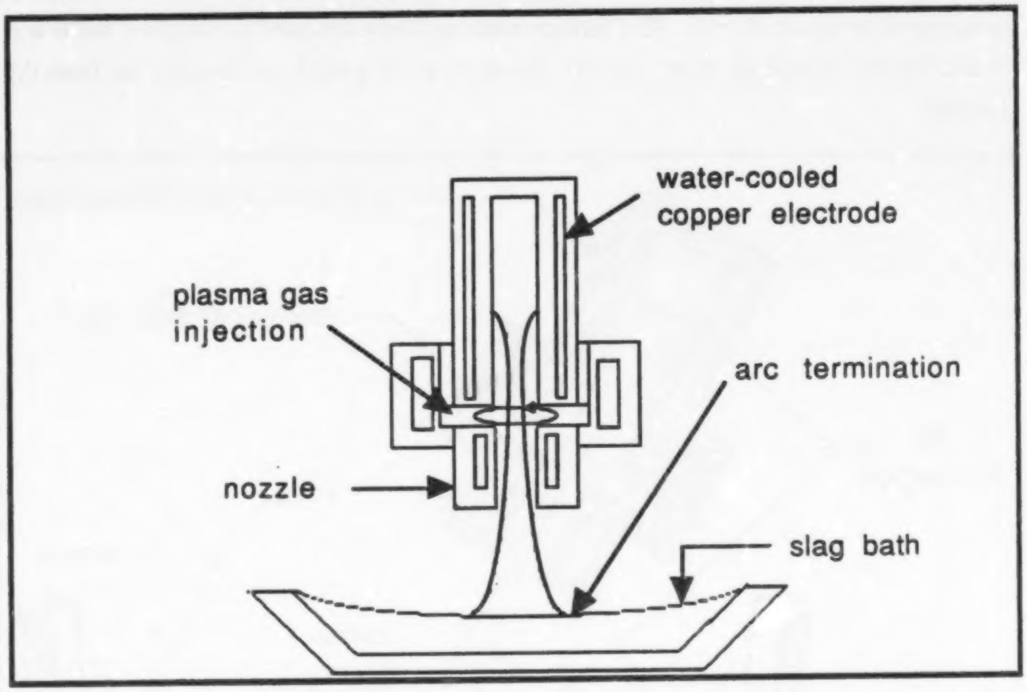


FIGURE 1: Schematic of the quarter-scale reactor showing the orientation of the plasma torch with respect to the rotating tub.

PHASE II (1986-1988):

The first plasma centrifugal reactor was developed with a 150 kW transferred-arc plasma torch operating on air or oxygen-argon mixtures. The furnace design incorporates a stationary plasma torch with a revolving tub (45.7 cm ID-18 inches) inside a sealed reaction chamber. The centrifugal force imposed upon the molten material moves it to the outside of the chamber, where mixing of new feed material is accomplished. Figure 1 shows the orientation of the plasma torch with respect to the revolving tub.

Operating with an oxidizing environment greatly reduces the sooting associated with straight pyrolysis. Tests were run with a number of feedstocks after completing assembly and debug in July, 1987[2]. Liquid feeds such as water, methanol, and fuel oil were fed at uniform rates. A spoon feeder permitted adding dirt or dirt and hydrocarbon mixtures (polymers and such) in 0.5 to 1.0 kg quantities every 5 to 15 minutes. An effluent gas treatment system which includes a quench spray followed by a rock tower was used to cool, neutralize and separate particles from the acidic exit gas. An air-ejector located in the exhaust duct was used to maintain the furnace pressure below atmospheric. Tests showed that the non-volatile components retained in the vitrified mass are non-leachable as determined by standard tests. This furnace was originally designed to 'tilt-pour' but it was found that the molten glass became too viscous to allow pouring of the material from the furnace.

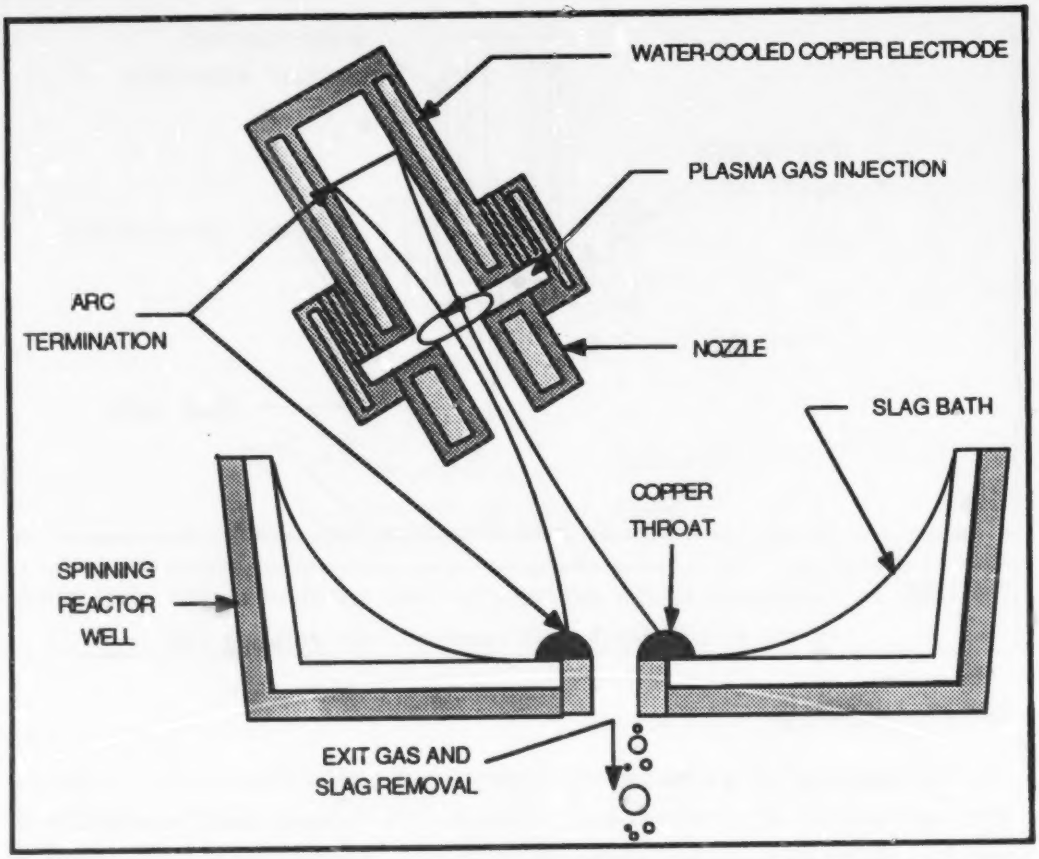

WATER-COOLED COPPER ELECTRODE
PLASMA GAS INJECTION
ARC TERMINATION
NOZZLE
SLAG BATH
COPPER THROAT
SPINNING REACTOR WELL
EXIT GAS AND SLAG REMOVAL

FIGURE 2: **Schematic of the demonstration reactor showing the bottom pour configuration for exit gas and molten glass.**

Work with the quarter-scale reactor resulted in the EPA selecting the PCR for inclusion in the second round of the SITE program. We decide to design a larger reactor for the demonstration program (Phase III), using the insights gained from the quarter-scale reactor tests.

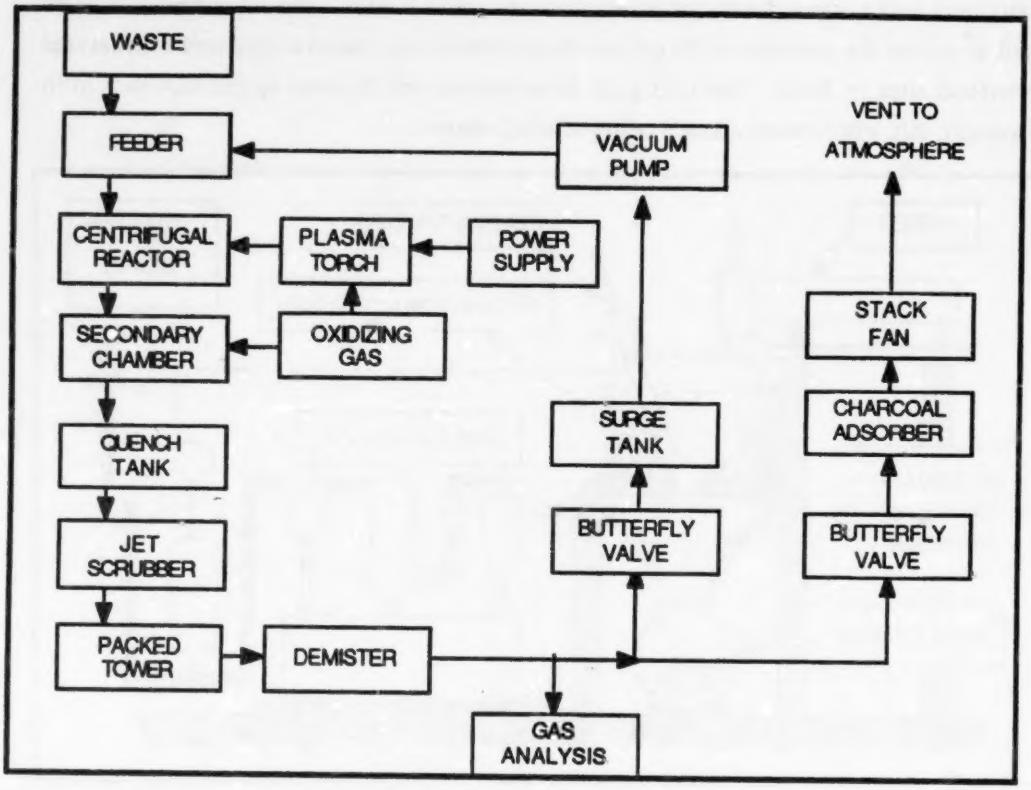

WASTE
FEEDER
VACUUM PUMP
VENT TO ATMOSPHERE
CENTRIFUGAL REACTOR
PLASMA TORCH
POWER SUPPLY
SECONDARY CHAMBER
OXIDIZING GAS
STACK FAN
SURGE TANK
CHARCOAL ADSORBER
QUENCH TANK
JET SCRUBBER
BUTTERFLY VALVE
BUTTERFLY VALVE
PACKED TOWER
DEMISTER
GAS ANALYSIS

FIGURE 3: Block diagram of the PCR-6

PHASE III (1988-PRESENT)

Design of a large PCR was started in late 1987. This reactor was dubbed the PCR-6 since it had a 6 foot diameter reactor tub. The design incorporated a bottom port for both exit gas and molten glass Melt chamber geometry is shown in figure 2. Figure 3 displays a block diagram of the major components of the PCR-6. The reactor section consists of a feeder, primary chamber, rotary throat, drive mechanism, secondary combustion chamber and the glass collection chamber. The gas treatment system consists of a quench tank, jet scrubber, packed bed scrubber, demister, activated charcoal adsorber and a stack blower. Figure 4 shows a schematic diagram of the system elements.

PCR-6

Hazardous waste is initially loaded into a feeder. Depending on waste type, it may be a screw, Archimedes spiral or a conveyor. In the Preliminary Tests for the EPA, specially prepared, spiked soil known as Synthetic Soil Matrix (SSM) was charged from 5 gallon containers into a screw feeder or an Archimedes spiral feeder. The latter feeder will be used to accept the contents of 55 gallon drums containing contaminated soil from actual superfund sites in Butte. The next generation reactor will be even larger (2.4 to 3 m in diameter); this will accommodate feeding of whole drums.

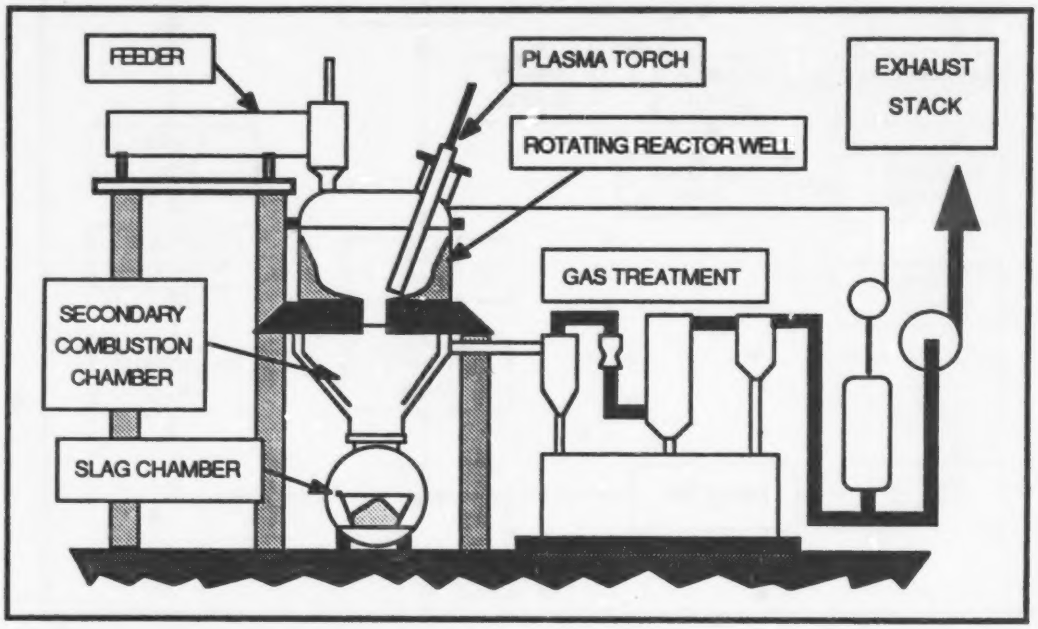


FIGURE 4: **Schematic of PCR-6 showing the feeder, primary and secondary chambers and the gas treatment system.**

During feeder loading operation, a plunger valve isolates the feeder from the hot reactor, Air is purged through the feeder into the reactor to insure that no toxic vapors are present upon opening the feeder door. Once loading has been accomplished, the feeder is sealed from atmosphere and the plunger valve is opened to access the waste material into the reactor.

The reactor itself consists of three chambers: a primary reaction chamber in which the plasma torch is located, a secondary chamber where incomplete combustion products react with supplementary oxygen to form water and carbon dioxide and a chamber where the molten glass is collected. Inside the upper chamber is a rotating tub about 1.8 m (6 ft.) ID, which spins at about 40 rpm. The plasma torch provides one termination of a DC arc, with the other termination being initially the copper throat of the rotating tub. The walls of the tub are lined with refractory material and a "skull" consisting of solidified waste material (vitrified soil) built up during previous runs. The skull begins to melt under the action of the torch and eventually becomes a conducting medium. When the waste material becomes sufficiently molten to be able to conduct, the plasma torch can be adjusted to move away from the copper throat and onto the molten glass. This process continues most of the surface of the rotating tub has been treated and turned to glass. When all of the waste material in the rotating tub has been treated, the feeder is started and new waste material is fed into the reactor. During feeding, the reactor is rotated at sufficiently high speeds to keep the new feed material from rolling down to the throat of the rotating tub.

The waste material that is fed into the reactor falls into the existing melt and is itself melted by interaction with the plasma. Any organic contaminants that the waste contains will be vaporized and burned in the oxidizing atmosphere of the upper and lower chambers. The inner core of the plasma column can reach temperatures of over 10,000°C which maintains the ambient temperature in the upper chamber above 1000°C. At such temperature, organic vapors that have been released from the waste will immediately burn when mixed with the hot oxygen rich furnace atmosphere.

Feeding continues until material build up causes the glass to reach the point of flowing into the copper throat. The feeder is turned off and time is allowed to complete the removal of any organic material. This is determined by the change in oxygen level in the exhaust and the clearing of soot as observed in the upper chamber. Upon completion of vaporization and melting of the waste, the speed of the revolving reactor tub is slowed. Rotating the tub at speeds of 5 to 10 rpm will allow gravity to overcome the centrifugal force on the molten glass and allow it to flow through the center hole, falling through the secondary chamber to be collected in the chamber below. The molten glass is collected in a pig mold where it later solidifies. After the molten glass has been tapped the rotational speed of the reactor is increased to resume the process. Presently the glass is allowed to cool in the collection chamber. In the future, an air lock will facilitate the replacement of the full glass mold with a new one to allow uninterrupted operation. The process, treating wastes, reacting organics, casting glass and then resuming treatment continues until a planned shutdown. Shutdown consists of turning off the plasma torch, allowing time for the molten material in the reactor tub to solidify to form the refractory layer for the next operation, and then stopping the tub rotation.

During the melting process, gases move out of the primary chamber through the throat into the secondary chamber. If combustion of the organic material is not complete in the primary chamber, additional O_2 is injected into the secondary chamber in the vicinity of the throat to cause further combustion, which is completed before the gas flows around a baffle and out into the gas treatment system. Gas temperature in the secondary chamber reaches at least 500°C. Since the exit duct is refractory lined, exhaust gas arrives at the quench tank at nearly the same temperature. Since air is used as the source gas for the torch, the gas stream will be acidic due to the formation of NO_x from the reaction of N_2 with O_2 at the high temperatures of the plasma. HCl formed from the break down of chlorinated hydrocarbons will also add to the gas acidity. Other gases in the exhaust will include the combustion products CO_2 and water vapor, plus excess O_2. In the event that combustion is incomplete, CO will be formed. If CO levels are considered to be excessive, the system will be placed into a recirculation mode as discussed below.

There are several cooling circuits associated with the furnace. The torch circuits are cooled by a high velocity distilled water system. This system is closed loop, consisting of a water pump, heat exchanger, flow interlocks for each circuit and a pump discharge filter. All parts of the rotating reactor well exposed to high temperatures are cooled by a glycol-water system similar to the distilled water system described above. The remaining cooling requirements for the furnace are met by circulating water from an open loop building system. These circuits include the reactor lid, reactor chamber upper (non-rotating) wall, secondary chamber walls, collection chamber and hydraulic system.

GAS TREATMENT SYSTEM

The gas treatment system consists of four parts: scrubber, sampler, recirculation and exhaust. The scrubber is composed of four separators, two pumps and a tank. The sampling system includes a pump and monitors for CO_2 and O_2. Recirculation consists of a surge tank and a water ring vacuum pump. Exhaust system is comprised of ducting, a charcoal bed and an exhaust blower.

The gas stream exits the reactor via the secondary chamber exhaust duct. The gas then enters the scrubber where it first passes into a quench tank encountering a fine spray of a mild caustic solution (NaOH). This solution is intended to react with the acidic components of the gas and neutralize them. The caustic solution is circulated through scrubber elements by means of two high pressure pumps. The quenched gas is then directed into the jet scrubber, which is designed to reduce the particulate load in the gas. From the jet scrubber the gas enters the bottom of a packed bed tower. The packed bed consists of one inch pall rings with a spray at the top of the column. The gas is then drawn into the demister which is a dry packed bed.

After leaving the demister the gas enters a serpentine duct constructed for sampling equipment. The distances between and location of the ports were determined by the requirements of the various analytical samples to be taken. One sample train is used for control. A diaphragm pump delivers the gas sample to O_2 and CO monitors. The O_2 and CO levels help determine the effectiveness of combustion. Excessive CO levels will require activation of the emergency bypass valve allowing the system to go into recirculation to prevent the release of toxic vapors. The initial set point for CO level will be determined during further testing.

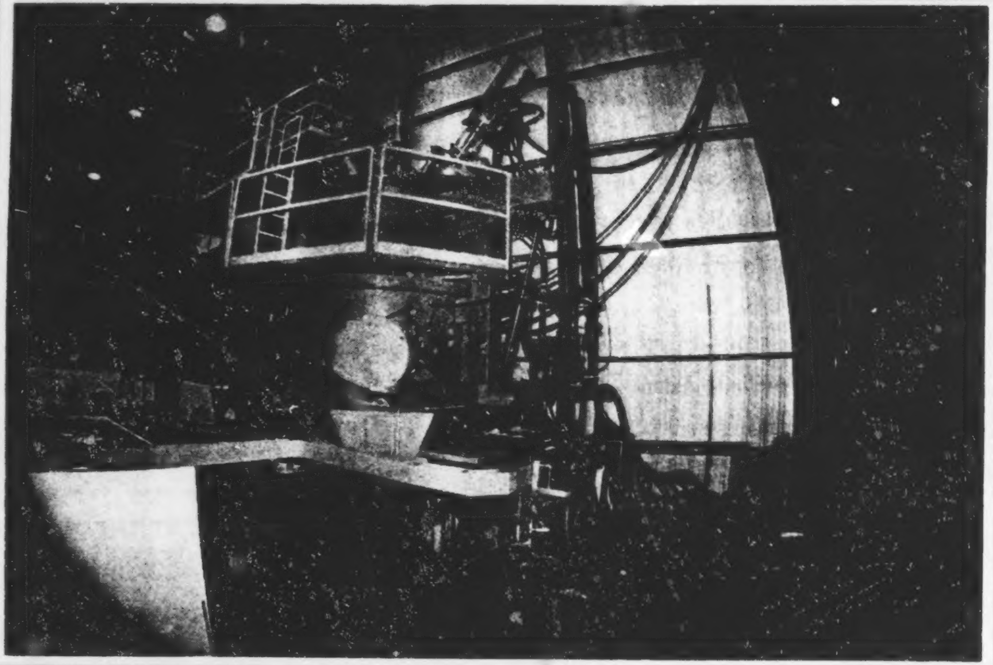


FIGURE 5: Photograph of the PCR-6 installed in the Ukiah lab.

The recirculation system includes two air operated ball valves which respond to a signal from the control panel. Under normal conditions the valve to the exhaust stack is open and the valve to the surge tank is closed. During operation the surge tank is kept evacuated by the water ring vacuum pump. Upon initiation of recirculation, the valve to the stack closes and the valve to the surge tank opens. There is enough volume in the surge tank to operate for about 5 minutes, time enough to correct a problem. If the abnormal CO levels persist after 5 minutes the system would be shut down.

Following the recirculation system the gas enters the exhaust stack blower which is capable of producing 80 in. of H_2O at 100 cfm. At the outlet of the blower is a charcoal bed adsorber to remove any residual organics not detected by the sampling system. It was found during the preliminary tests that the charcoal adsorber became loaded with condensate, rendering it useless as a gas adsorber. Therefore it has been removed from the system. A stack blower raises the gas pressure to atmosphere for release.

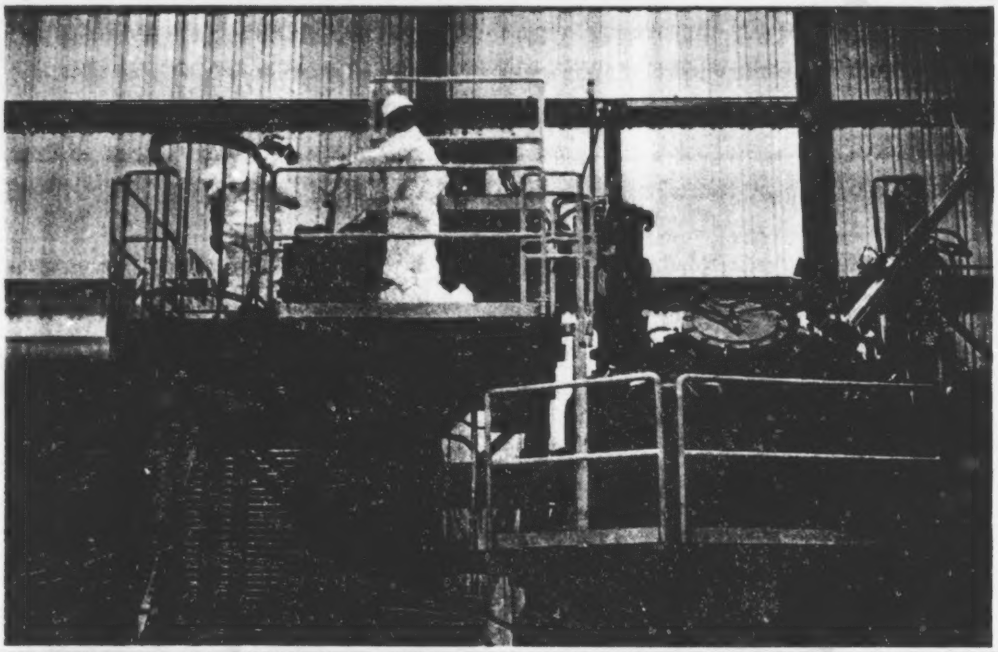


FIGURE 6: Photograph of PCR-6 showing the feeder, plasma torch and primary melt chamber during feeder reloading operation.

TEST RESULTS

A photograph of PCR-6 installed in the Ukiah lab is shown in figure 5. This picture shows the layout of the facility. The closed cooling water systems can be seen in the lower right hand corner. The plasma torch can be seen protruding from the top of the reactor. The primary melt chamber and drive chamber are the main features of this photograph. Figure 6 gives a good view of the plasma torch and feeder. The operators are in the process of placing material into the feeder. During the operations with the spiked SSM the feeder deck was an exclusion area while the surrounding space in the reactor room was a control area. The off-gas treatment system is shown in figure 7; the large tank to the left is the surge tank while the components in the center of the picture comprise the gas treatment system.

Shakedown tests with the PCR-6 were completed using local soil and oil (15% by weight). These tests were done before and after the preliminary tests for the SITE program. During these tests we were able to feed up to 200 lbs/hr of oil and soil. Initial runs were performed using argon as a torch gas. The argon arc proved to be unstable in the current configuration because of the interaction of the plasma with the chamber atmosphere. It was found that high moisture contents caused this instability. Further testing showed that air was a much more stable plasma gas when interacting with the furnace atmosphere. The plasma torch will operate satisfactorily with air as a plasma gas at arc currents up to 1200 amperes at 400 to 600 volts. In cases where the moisture content was low the plasma torch was able to operate with argon gas at up to 1200 amperes and 400 volts. Use of O_2/argon mixtures as plasma gas proved unsatisfactory due to shortened electrode life.

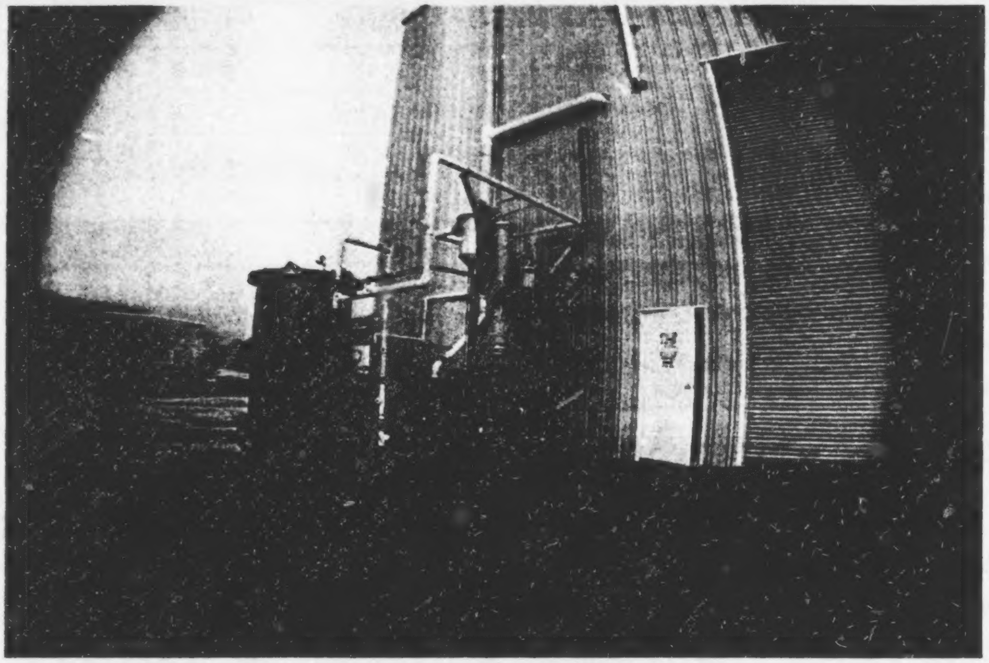


FIGURE 7: Photograph of PCR-6 exhaust gas treatment system.

Preliminary tests for the EPA SITE program were run using Synthetic Soil Matrix (SSM) (both unspiked and spiked material) (See Table 1) which was prepared by Enviresponse, Inc. Preliminary Test #1 was performed on 20 April, 1989 using argon as a torch gas on 550 lbs of unspiked SSM. The second preliminary test was conducted on 25 April on 300 lbs of spiked SSM using air as a torch gas. The third preliminary test was conducted on April 26. An air plasma was used to treat 200 lbs of spiked SSM. Continuous Emission Monitoring (CEM) was performed during both shakedown and preliminary tests. Data taken by the CEM included the levels of O_2, NO_x, CO, and THC (Total Hydrocarbons).

For the final preliminary test, samples were taken on the exhaust gas, which included Volatiles/Semivolatiles, Particulate matter, Velocity/Volumetric Flow Rate (Method 1&2), Fixed Gases (Method 3), Moisture (Method 4), Flue Gas-Metals (Method 12), and HCl. Samples were also taken from the slag, the feed material and scrubber water.

SYNTHETIC SOIL MATRIX (SSM)	
COMPONENT	WEIGHT %
Sand	31
Gravel No. 9	6
Silt	28
Topsoil	20
Clay	15
SPIKING MATERIALS	
COMONENT	mg/kg - ppm
Tetrachloroethylene	3,277
Anthracene	7,361
Bis (2-ethylhexyl) phthalate	3,702
Chromium	1,898
Zinc	28,306

Table 1 **SYNTHETIC SOIL MATRIX (SSM) composition both spiked and unspiked.**

Most important to the development of the PCR was the ability of the reactor to vitrify soil and transfer that glass to a collection chamber. The bottom pour arrangement was proven during the shakedown tests. As shown in figure 8, it was possible to produce a fairly large area of molten glass. After an operating procedure was established it was possible to slow the reactor speed and pour glass from the melt chamber into the collection chamber. A representative sample of the glass is shown in figure 9. The slag produced during the preliminary tests was similar to that shown. At the time of this writing the results of the leach tests were not yet available.

CEM results during shakedown tests on local soil indicated high levels of NO_x (up to 15,000 ppm) on runs when air was used as a torch gas. This level of NO_x amounts to less than 1 lb/hr at the system gas flow rate (~70 cfm). However, it was found that the level of NO_x dropped significantly (to 5000 ppm) when processing soils with organics (oil) added. This can be explained due to the competing reactions involved in the formation of combustion gases and NO_x. During the shakedown tests the level of oxygen followed the feeding patterns for soil with high organic loads as would be expected. Shortly after commencing feed, an indication of lowering O_2 levels was observed. This is an indication of a reaction (combustion) between the decomposed hydrocarbons and O_2. Additional O_2 was injected into the melt chamber during subsequent runs to maintain an excess of O_2. During tests with excess O_2 maintained, a green colored flame was observed protruding from the secondary combustion chamber into the collection chamber. This was a positive indication of combustion in the secondary chamber.

Tables 2,3 and 4 give the CEM results for the three preliminary tests. P-1 was performed with argon as a torch gas and unspiked SSM, therefore no additional O_2 was needed. The CEM results were consistent with this type of operation. The O_2, CO_2, CO and THC were low for the duration of the test as expected since no free O_2 or hydrocarbons were introduced. There were however some startup spikes as shown by the 1-min max results, which at this time cannot be explained. Levels of NO_x produced were attributed to purge air from the feeder and collection chamber and small air leaks into the system.

PCR-6, P-1 CEM RESULTS

MONITOR	1-MIN MAX	1-MIN MIN	1-MIN NORM
O_2 (%)	6.3	0.6	1.7
CO_2 (%)	18.1	0.2	4.0
NO_x (ppm)	4952	1045	3500
CO (ppm)	1003	0	4
THC (ppm)	115	4	6

Table 2 CEM results from preliminary test #1, performed on April 20, 1989 using argon as a torch gas.

Spiked SSM and air torch gas were used during P-2, in which 300 lbs of material was treated. No additional O_2 was added during this test in order to determine a base level of additions for P-3. Levels of O_2, CO_2, CO and THC were all higher than in P-1 as expected. Since air was used as a torch gas, the NO_x levels were higher in this case but not to the levels observed when using air and unspiked soil. The O_2 level dropped to 6.2 % during feeding operation. It was decided to try to maintain the level at ~ 13 % for P-3 during feeding to try to insure complete combustion. Unexplainable CO spikes still occurred, even when not feeding. One explanation for the CO spikes might be a periodic leak of ethylene-gylcol (cooling medium) from the copper throat area. The throat area had been a source of leakage during shakedown tests.

Near the end of P-2, it was determined that there was enough slag buildup to facilitate a pour. The reactor speed was lowered and ~100 lbs of glass was tapped. Samples of the slag were taken for analysis but the results were unknown at the time of this paper's writing. A photograph of slag (from a later test) similar to that collected in P-2 is shown in figure 9. The slag that has been collected to date appears to glassy in nature and well mixed. There have been problems with non-treated material passing through the throat, but this has been alleviated through a feeder modification.

PCR-6, P-2 CEM RESULTS

MONITOR	1-MIN MAX	1-MIN MIN	1-MIN NORM
O_2 (%)	15.5	6.2	14.0
CO_2 (%)	18.0	1.2	3.0
NO_x (ppm)	7808	4315	5000
CO (ppm)	>10000	176	230
THC (ppm)	333	48	60

Table 3 CEM results from preliminary test #2, performed on April 25, 1989 using air as a torch gas.

Supplemental O_2 was added during feeding operation for the P-3 test. This resulted in higher normal levels of O_2 and CO_2 and lower normal levels of CO and THC, as compared with P-2. NOx levels were about the same as in P-2, but higher than had been seen in previous tests with higher levels of organics. The SSM used in P-2&3 contained only 1% organics, not enough to have an impact on the NO_x levels. This test consisted of feeding 200 lbs of SSM, which is not a large amount of material considering that the system had been drained the night before. It was because of this that it was difficult to obtain a representative sample of slag from P-3; not enough material had been treated to obtain a good pour.

Preliminary results by Radian indicate that DRE's of 0.9999 to 0.99999 were obtained. High levels of organics were found in the slag from P-3 due to untreated material being thrown down the throat by the feeder. This was only discovered as a problem at the time of the P-3 test (the feeder was subsequently modified).

PCR-6, P-3 CEM RESULTS			
MONITOR	1-MIN MAX	1-MIN MIN	1-MIN NORM
O_2 (%)	18.4	12.9	17.5
CO_2 (%)	9.8	0.1	0.2-4.0
NO_x (ppm)	6536	4652	5500
CO (ppm)	375	17	50
THC (ppm)	194	16	25

Table 4 CEM results from preliminary test #3, performed on April 26, 1989 using air as a torch gas.

CONCLUSION

Based on the information gathered to date, the PCR project has reached some degree of success. The major objectives of the system have been accomplished, in that heavy metals and organic wastes have been treated with favorable results. Hydrocarbons have been broken down and reacted with O_2 to produce CO_2 and H_2O. Molten slag has been poured from the reactor and collected. To date, all results indicate that these objectives have been reached with a high degree of success.

Improvements will be made to this reactor (PCR-6) before the EPA SITE demonstration. The seals around the copper throat will be improved. This will allow higher heat loads in the area of the throat during feeding to insure total treatment of the toxic material. Investigations are proceeding to increase the power input into the melt chamber. Modifications are being planned to enable higher feed rates (up to 600 lbs/hr). This will require more advanced slag handling techniques to provide for increased amounts of molten glass. Materials of construction for some components will be changed to resist the acidic attack of the NO_x and HCl. Modifications to the scrubber system will be required to handle the higher gas loads.

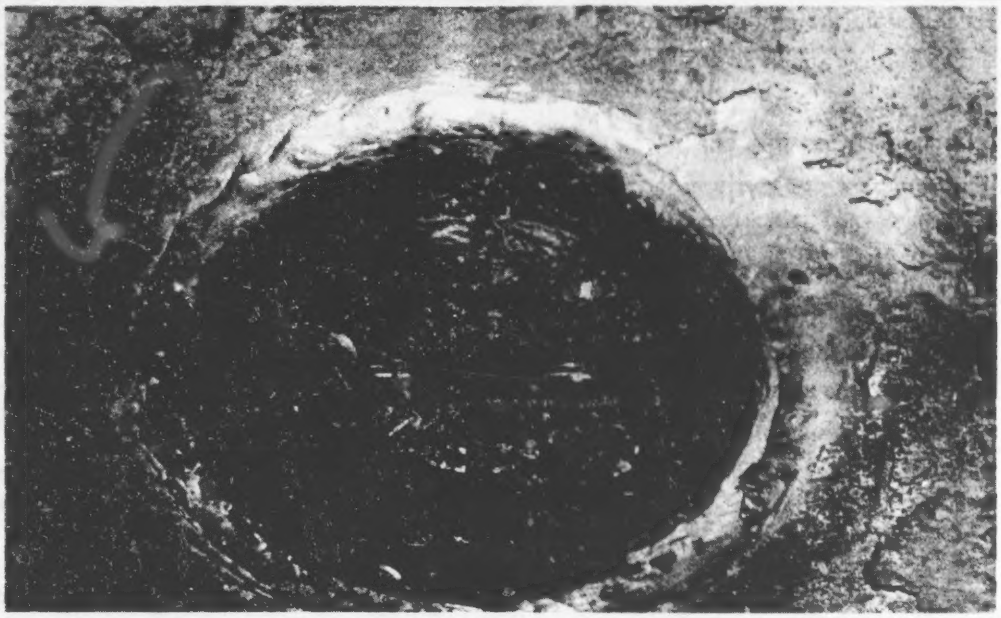


FIGURE 8: Photograph of PCR-6 melt chamber showing the extent of the molten material.

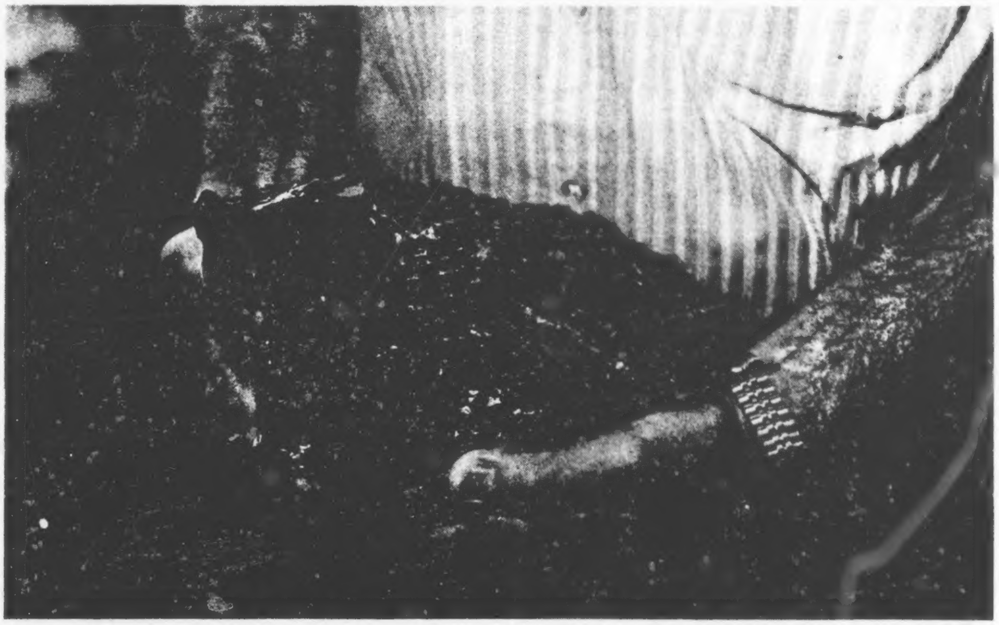


FIGURE 9: Photograph of vitrified slag from local soil and 15% oil.

At this time the equipment is being disassembled and sent to Butte, MT. for a SITE demonstration scheduled for the summer, 1989. The feed for the demonstration tests will be a mixture of mining wastes (soil containing heavy metals) and wood-treating waste oil (containing pentachlorophenol and other components). Feed rates of 100 lbs/hr for 6 hours are to be performed for the SITE test. It is planned to operated the plasma torch with air at power levels of 600 volts DC and 1000 amps. O_2 will be added to both the primary melt chamber and the secondary chambers during feeding operations. It is planned at this time to feed at rates of 200 lbs/hr for 30 minutes and treat the material for 30 minutes while reloading the feeder, then feed again during the 6 hour period. Six hundred pounds of material will be enough to produce a reasonable slag pour. Results from the demonstration will be available in report form about six months after the three planned replicate runs are made.

After the EPA SITE test, it is planned to continued operations in Butte under the direction of the DOE to further evaluate the PCR. A separate program has been established for this work. Optimum feed rates and power levels will be investigated during these tests on a variety of materials. The long term goals of the DOE are to process low level radioactive wastes. Efforts to implement this technology will be provided by personnel at the Idaho National Engineering Laboratory (INEL).

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HAZCON, INC.
SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION
FINDINGS AND CONCLUSIONS

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INTRODUCTION

In October, 1987, the U.S. Environmental Protection Agency's Offices of Research and Development (ORD) and Solid Waste and Energy Response (OSWER) initiated their first test of a solidification/stabilization (s/s) process under the Superfund Innovative Technology Evaluation (SITE) program. The technology demonstration was developed by the founders of HAZCON, Inc., based in Texas.

The HAZCON solidification process was selected for its potential to effectively stabilize and solidify wastes containing high concentrations of organic contaminants. High organic wastes inhibit the reaction mechanisms of most s/s processes, and thus had rendered the technology non-effective as a pretreatment alternative for land disposal of these wastes.

The major objective of the demonstration was to develop reliable cost and performance data on the HAZCON process so that it could be adequately considered in Superfund decision making. Evaluation criteria were established jointly by the EPA and HAZCON to evaluate the effectiveness of the process in immobilizing contaminants and in increasing matrix integrity.

The Douglassville, Pennsylvania National Priority List (NPL) Site, a former oil reprocessing facility, was selected as the test site. The site was placed on the NPL in 1985 due to the presence of high levels of organic and inorganic contaminants. Contaminants include PCB's, heavy metals, volatile and semivolatile organics, base neutral acids and other toxic materials. An estimated 250,000 cubic yards of material may be contaminated.

PROGRAM OBJECTIVES

Five major objectives of the HAZCON SITE demonstration were to determine the following:

1. Ability of the stabilization/solidification technology to immobilize and solidify the site contaminants.

2. Effectiveness of the technology in treating wastes with contaminant concentrations varying over the range 1-25% by wt. oil and grease.

3. Performance and reliability of the process system.

4. Long-term stability and integrity of the solidified mass.

5. Costs for applying the technology to commercial size or Superfund sites.

METHODS AND MATERIALS

Contaminated soils from the site were processed by HAZCON's Mobil Field Blending Unit (MFU). The system is truck mounted and typically used by HAZCON for small field projects such as the SITE demonstration. The system holds, meters and homogenizes the waste feed with Portland cement, Chloranan (HAZCON's proprietary additive) and water. The processed material was then placed in 1 cubic yard-sized forms for curing.

Samples were collected both before and after treatment. These samples were subjected to an extensive testing protocol, to include TCLP leachate analysis, permeability, weathering and strength tests, and microstructural analysis. Materials from six plant areas were tested. Each area contained varying levels and types of contaminants across a variety of waste matrices. The following designations were used to refer to the six plant areas:

LAN	Lagoon Area North
LFA	Landfarm Area
PFA	Plant Processing Area
DSA	Drum Storage Area
FSA	Filter Cake Storage Area
LAS	Lagoon Area South

Five cubic yards of material were processed from each of the first five areas listed, twenty five cubic yards were treated from Lagoon Area South (LAS).

In order to effectively gauge HAZCON's claim to immobilize volatile organics, the EPA requested permission to inject toluene at 125ppm into the feed from DSA, PFA, and LFA.

Core samples were analyzed after 7 and 28-days of curing. These analysis were performed to determine the effects of time and weathering on the mass. This latter series of tests provides additional evidence of the long term stability of the HAZCON treatment process.

FINDINGS AND DISCUSSION

The six test areas offered a wide diversity of waste. The oil and grease ranged from 1% by weight at the DSA to 25% at FSA. Polychlorinated biphenols (PCBs) were detected up to 80 ppm by weight with the maximum concentration at LAS. Lead contamination concentration ranged up to 2.5% by weight. Volatiles and base neutral acid extractable (BNAs - semivolatiles) organics reached levels of about 100 ppm in some areas.

Permeabilities of the treated soil were very low, in the range 10^{-8} to 10^{-9} cm/sec. A value of 10^{-10} is generally considered an indication of an impermeable solid. Unconfined compressive strengths (UCS) ranged from about 200 psi for FSA to 1500 psi for PFA. These values are quite satisfactory from a load bearing point of view, i.e., equipment traffic.

TCLP leaching tests, the results shown in Table 1 are discussed below:

> Metals - the leachates for the solidified soils showed metal levels at or near the detection limits. The results were a factor of 500 to 1000 times better than the untreated leachates.

TABLE 1. RESULTS OF TCLP LEACHING TEST

Plant	Soil Concentrations, ppm			Leachate Untreated Soil, mg/l			Leachate Treat Soil - 7 days, mg/l		
Area	Lead*	VOC+	BNA°	Lead	VOC	BNA	Lead	VOC	BNA
DSA	3,230	ND¶	12	1.5	0.9§	ND	0.015	0.40	0.055
LAN	9,250	2	21	33.	0.03	1.02	0.002	0.02	1.340
FSA	22,600	150	534**	18.	1.03	2.86	0.07	0.74	3.910
LFA	13,670	ND	37	28.	5.90	0.01	0.04	0.23	0.040
PFA	7,930	0.4	18	22.	1.80	0.01	0.01	0.40	0.090
LAS	14,830	6	40	53.	0.07	0.01	0.014	0.06	0.470

* The great majority of the metals is lead.

+ Primarily Toluene, trichlorethene, tetrachloroethene, ethylbenezene, xylenes.

° Phthalates, phenols, naphthalene.

¶ ND - not discernable

§ Toluene was injected into untreated soil samples for DSA, LFA, and PFA before performing TCLP. Concentration injection equal to level measured in 7 day solids.

** Very high in naphthalene and phenols.

Volatiles - the primary compounds detected were trichloroethene, tetrachloroethene, toluene and xylenes. Only the leachates for the untreated soil and 7-day cores were analyzed. The levels of leachable contaminants were approximately 2 to 20 times less in the treated materials than the untreated leachates.

BNAs - the compounds detected in the leachate were phthalates and phenols. The phthalates were reduced to near their detection limits of .010 mg/l in both the treated and untreated soil leachates. The total phenols in the leachates were in the range of .030 to 3.85 milligrams per liter, with the same concentration levels seen in both the untreated and treated soil leachates.

PCBs - were nonquantifiable in the leachates.

CONCLUSIONS

The following conclusions were drawn by the EPA and their subcontractor Enviresponse, Inc. upon reviewing the data on the HAZCON process. They are:

o The process can solidify contaminated material high in organics. Soils at the Douglassville Superfund site with up to 25% organics were solidified. Other applications showed successful solidification of petroleum refinery waste streams, organics, water high in organics from a waste storage pond, metal finishing sludge, and other less clearly defined wastes.

o Immobilization of heavy metals was observed, with leachate improvements for lead and zinc in excess of a factor of 100.

o Organic contaminants, VOCs and BNAs, were not immobilized for the most part. The extensive testing for the Demonstration Test and other test programs showed no immobilization of the organics. However, there were two instances where immobilization of organics occurred.

o The physical properties of the treated wastes are in general quite satisfactory. High UCS, low permeabilities, and satisfactory results of weather tests were obtained. However, large volume increases in treated soils can be expected, and the microstructural analyses of the solidified soil materials indicates a potential for long-term durability problems.

o Application for immobilization of heavy metals (up to 2.3% by wt.) in wastes containing high organics, up to at least 25% by wt oils, has been shown. Successful immobilization of higher quantities of heavy metals at even higher oil and grease levels would be anticipated.

o Immobilization of VOCs and BNAs did not occur in the SITE Demonstration test on soils up to 25% by wt oil and grease, and immobilization of other organics, as reported by other investigators, was also unsuccessful. However, immobilization of some petroleum refinery wastes was successful.

o Therefore, applications for immobilizing organic contaminants, compared to a simple solidification process with only cementitious materials, may have to be tested on a site-by-site basis to prove applicability of the HAZCON process. For high organic content wastes, solidification may be very difficult; the use of Chloranan will enhance solidification of organics.

The estimated cost for commercial scale application of the HAZCON process was not reported in the Demonstration Final Report. Instead a figure of $205 per ton of contaminated soil was reported, representing the estimated per ton cost of the 50-cubic yard demonstration. This is much higher than the normal $50 to $65 per ton costs HAZCON has charged clients in the past for commercial scale application.

One final observation made by this writer during the demonstration and subsequent interpretation of the data is that the use of EPA contracted support services in the performance of this and other SITE evaluations may introduce an element of bias to the program. An element which, either for or against the demonstrated technology, will distort the true advantages and/or disadvantages of the technology being evaluated, thereby corroding the credibility of the entire SITE program. Inaccurate and misleading interpretation of the data from this test has been observed, and conclusions have been published which can not be supported. One EPA contracted party involved in this evaluation now operates a solidification/stabilization firm.

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SITE: Fixation of Organic and Inorganic Wastes/ Intimate Mixing Technique

by

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SITE: Fixation of Organic and Inorganic Wastes/ Intimate Mixing Technique

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I. INTRODUCTION

Solidification/Stabilization of industrial solid waste, particularly wastes classified as hazardous and toxic under current U. S. EPA rules and regulations is a developing technology. Physical/chemical processes involving the use of pozzolans or cements with the addition of various special additives are the most prevalent. These processes may be applied to the waste in-situ or the waste can be removed, treated, mixed using an intimate mixing system and then replaced or removed to another repository. The Soliditech process described in this paper is an intimate mixing process based on the use of pozzolans or cement and various additives, especially URRICHEM, that enhances the ability of the mixture to incorporate organic compounds into the matrix and reduce the potential for these compounds to leach from the mass.

II. BACKGROUND INFORMATION

Soliditech, Inc., is a Houston, Texas based company established to apply the solidification technology described herein to the remediation and cleanup of abandoned disposal facilities and sites and to the treatment of currently generated wastes. Soliditech, Inc. is a wholly owned subsidiary of United Resource Recovery, Inc., which is a new waste disposal company that will incorporate the solidification process at a new facility to be constructed in the near future.

Soliditech submitted the proposal to the U S. EPA to demonstrate the technology under the Superfund Innovative Technology Evaluation (SITE) program in 1987. The proposal was accepted and ultimately a demonstration site selected which is located in New Jersey. The site is the Imperial Oil Company site in Morganville, New Jersey, some twenty or thirty miles south, southeast of Newark. The site has been in existence since the early 1900's and has been used for several purposes from food processing to recycling oil which is its current purpose. (See Figure 1). Various waste streams are present at the site most of which include some form of petroleum hydrocarbons in a matrix of soil, filter media or as a tank bottom sludge.

The field demonstration was conducted the first week of December, 1988. Three different waste streams were treated as part of the demonstration which included a soil contaminated with oily sludge, a filter media with a high percentage of hydrocarbons and an oily tank bottom sludge. The latter stream was co-treated with the filter media during the demonstration. A total of fifteen yards of treated waste was collected, sampled and tested. The waste was placed in plywood forms which were removed after 28 days. The waste blocks were stacked on a protective sheet of HDPE and covered with additional sheets for protection and storage long term. Sampling, testing and observation of the blocks will continue for five years.

III. PROJECT DESIGN

The Soliditech process is designed to solidify waste materials by mixing the wastes with a chemical reagent, various additives, and pozzolanic materials. The following subsections describe the Soliditech process chemistry, treatment process, and the main components of the process.

Soliditech Technology

The Soliditech process solidifies wastes by use of URRICHEM (a proprietary chemical reagent, U.S. patent pending), additives, pozzolanic solids, and water. The proportions of reagent, additives, and pozzolan are optimized for each particular waste requiring treatment. The solidified material displays properties of excellent unconfined compressive strength, high stability, and a rigid texture similar to that of concrete.

The waste material to be treated is first passed through a screen with 4-by 4-inch openings to remove large rocks, debris, or other materials. This screening step is performed to ensure that laboratory samples do not include large rocks. During normal operations, only very large material would be removed prior to treatment. The oversized material is collected and drummed for off-site disposal. Following screening, the waste material to be treated is placed in the Soliditech mixer, where the reagent and other additives are dispersed throughout the waste material. The reagent and additives aid in the chemical and physical immobilization of the hazardous constituents contained in the waste. It is sometimes necessary to add water to the waste material to achieve the proper moisture level and to achieve uniform blending of the raw waste material.

The waste mixture is then blended with pozzolanic materials. Pozzolanic materials are siliceous or siliceous and aluminous materials that inherently possess oxides (lime) to form compounds possessing cementitious properties. Pozzolanic materials that may be used in the solidification process include Class C or F flyash, cement kiln dust, slag cement, portland cement, and steel baghouse dust. Depending on the pozzolanic material used, calcium oxide (or its hydrated form, calcium hydroxide) may have to be added to assure a hard set. (Portland cement was used for the demonstration).

Hazardous compounds are immobilized by one or more of the following processes: encapsulation, adsorption, and or incorporation into the crystalline structure of the solidified material. The waste may actually penetrate any porous structures of the pozzolans as well as by bonding to the surface of the pozzolans by either ionic attraction or electrostatic forces.

Water contained in wastes that are treated by the Soliditech process and water added during the processing are involved in at least two types of reactions.

- Hydration reactions
- Equilibration with the environment through evaporation

The Paint Filter Liquids Test (SW-846, Method 9095, U.S. EPA 1986) which Soliditech routinely performs has shown that no free liquid remains once the solidification processing is complete.

As each solidification mixture is optimized for a specific batch of waste material and because considerable variability can exist between types of pozzolans, each batch of treated waste material is potentially unique. All results from this demonstration should be considered to reflect on the particular formulations and pozzolans used for the demonstration.

Treatment Process

The treatment system of the Soliditech process is presented in Figure 2. The treatment system, consists of a self-powered, variable speed mixing unit mounted on a low boy trailer, a control box containing all mixer controls, a hoist to raise and lower the mixing unit, a vibrator to aid hopper clean out, a liquid reagent storage tank with a metered feed system, a hopper for storing and dispensing the pozzolanic solids, tanks for storing process water, and a metered gate for discharging treated waste material.

Three designated waste materials were treated during the demonstration: Off-Site Area 1 (soil contaminated with oily sludge, Waste Pile) (filter cake) and the Abandoned Tank (oily sludge).

For Soliditech demonstration process, a batch of contaminated soil from Off-Site Area One was collected, transported on-site by a licensed solid waste transporter, sampled, and stored in a lined and covered dump truck until it was to be treated. The waste pile material was sampled immediately prior to its treatment. Sludge from the abandoned storage tank was collected and sampled prior to treatment and stored in 55-gallon drums.

Immediately prior to treatment, each batch of waste material from Off-Site Area One and the waste pile filter material was weighed or its density and volume measured and transferred to the mixing unit by a front-end loader. Prior to treatment of the mixture of sludge and waste filter material, dry waste filter material was collected in a front-end loader, weighed or its density and volume measured, and placed in the mixing unit. The weight or volume and density of sludge in the drums was determined. The drums of sludge were lifted and poured into the mixing unit. Adding the solid waste filter material first minimized splashing of the liquid waste.

Once the contaminated waste material was in the mixing unit, a measured volume of URRICHEM liquid reagent was pumped into the mixing unit. Additives were measured and added to the mixer. The mixing unit was turned on and the URRICHEM and additives were thoroughly blended into the waste. When water was required for the mix, the amount was measured and pumped into the mixing unit.

After the waste material, reagent, additives, and water were thoroughly blended, the volume or mass of pozzolanic material was determined and, as required, was added to the mixing unit. Mixing requires a minimum of 20 to 30 minutes until all of the ingredients are thoroughly blended into a wet pasty mixture. The mixing unit was lifted by its hydraulic legs and the slide gate operated to dispense controlled quantities of the mix into the larger sample containers and empty, plastic-lined, plywood forms. As the forms were filled, samples of the treated material were collected.

After each demonstration run was completed, the operation was shut down and the process equipment was decontaminated using a high pressure water and steam cleaner. This water was collected and drummed for off-site treatment or disposal.

Test run data including information on material usage, weights, volumes and all operating parameters, were recorded and maintained in a field log by Soliditech personnel for each test run of waste processed.

To confirm the Soliditech records, EPA kept similar records containing similar information, as well as the time at which all operations were performed. The EPA run records included the results of the particle (sieve) size analysis for the treated material and the results of slump tests.

IV. TEST RESULTS

Three types of waste material and one control mix were treated as part of the demonstration. The control mix was a mixture of clean sand, concrete, pozzolan (portland cement), URRICHEM and other additives that were part of the waste stream formulation. The waste streams consisted of contaminated soil, waste filter cake material and oily sludge.

Untreated waste samples were collected for each test parameter from each of the three waste streams. These samples were analyzed for total chemical constituents, physical characteristics and the amount of solubles removed by leaching/extractions. The results allow a direct comparison of physical and chemical properties between the treated and untreated waste and a determination of effectiveness of the treatment process.

In addition to discharging the treated waste into large 1 - cubic yard plywood forms, numerous cylindrical sample containers or forms were filled with treated waste and allowed to cure 28 days. After curing, the small sample cylinders were shipped to the laboratories for analysis. The final product was a monolithic material with measurable structural strength. The wooden forms were removed and the waste monoliths were placed in an enclosed on-site storage area for long term monitoring. Long term studies will include a six month leaching test and performing other extraction procedures at various times up to five years after treatment.

The analyses of the samples collected before, during, and after the Soliditech demonstration are summarized in Tables 1 and 2, and discussed below:

- Untreated Waste -- Untreated waste from the site consisted of contaminated soil, filter cake, and filter cake/oily sludge. These wastes contained 2.8 to 17 percent oil and grease, with relatively low levels of other organic compounds. PCB (Aroclors 1242 and 1260) concentrations ranged from 28 to 43 mg/g; arsenic concentrations from 14 to 94 mg/kg; lead concentrations ranged from 650 to 2,470 mg/kg; and zinc concentrations from 26 to 151 mg/kg.

- Treated Waste -- The Soliditech stabilization process produced solidified waste with high structural stability and low permeability. UCS values ranged from 392 to 856 psi. Permeability values ranged from 8.9×10^{-9} to 4.5×10^{-7} cm/sec. Because of the cementitious additives in the Soliditech process, pH values of the solidified wastes ranged from 11.7 to 12.0. Arsenic concentrations ranged from 28 to 92 mg/kg; lead concentrations from 480 to 850 mg/kg; zinc concentrations from 23 to 95 mg/kg; and PCB (Aroclors 1242 and 1260) concentrations from approximately 15 to 41 mg/kg. Low concentrations of phenol and p-cresol were found in solidified filter cake and filter cake/oily waste samples. These compounds were not detected in the untreated wastes.

- Control Mixture -- The control mixture contained 20 mg/kg lead. PCBs, phenols, and cresols were not detected in the control mixture. The reagents used for the solidification could not be analyzed for phenol, o-cresol, and p-cresol because of the high alkalinity in the control samples. Low levels (0.06 ug/L, total) of volatile organic compounds were detected in the TCLP extract of the control mixture.

- Extract of Untreated Waste -- Arsenic, lead, and zinc were found in EP, TCLP, and BET extracts of the untreated wastes. No PCBs were detected in the TCLP extracts of the untreated wastes. Total concentrations of up to 1.3 mg/l of volatile organic compounds and up to 0.38 mg/l of semivolatile organic compounds were detected in the TCLP extract of the untreated waste. Oil and grease concentrations of 1.4 to 1.9 mg/l were detected in the TCLP extract of the untreated waste. Untreated wastes could not be tested by ANS 16.1.

- Extract of Treated Waste -- Significantly reduced amounts of metals were detected in the TCLP, EP, BET and ANS 16.1 extracts of the treated waste. No PCBs or volatile organic compounds were detected in the TCLP extract of the treated waste. Phenol, p-cresol, o-cresol, and 2,4-dimethylphenol were detected in the post-treatment TCLP waste extracts. Oil and grease concentrations of 2.4 to 12.0 mg/l were detected in the TCLP extracts.

V. COSTS

The cost elements identified in the demonstration provide a means to estimate the cost of solidification for a typical site remediation. The actual costs of the demonstrations are biased when reduced to a unit cost basis by the impact of mobilization, demobilization, sampling and testing, decontamination time, low utilization rates.

Cost elements identified in the demonstration include the following:

1. Mobilization/demobilization of equipment
2. Capital cost of equipment
3. Cost of materials and additives
4. Cost of labor
5. Analytical expenses
6. Health and safety training
7. General overhead expenses
8. Utilities

There are various methods of applying these costs to any particular project. The unit costs on the SITE demonstration would be extraordinarily high if all the costs were to be applied to the approximate 15 cubic yards of waste treated during the 5-day demonstration period. As a point of information, this cost would have been about $2700 per yard assuming all pertinent costs were allocated to the treated waste volume.

In an actual field cleanup or remediation situation, many of the identified costs would become insignificant when spread over the much larger volumes of waste treated. Assuming that most factors would remain relatively constant, that the range of pozzolan cost was between $25/ton and $70/ton and that the throughput was about 15 cubic yards and 30 cubic yards of waste per hour, then the relative cost of the process would be between $46/yard and $75/yard for about 10,000 yards and $29/yard and $58/yard for about 100,000 yards of waste respectively. These numbers are for illustrative purposes only to reflect the impact of waste quantity on unit cost. It is important to point out also that these costs do not reflect waste handling costs prior to treatment and do not reflect post-treatment handling and disposal costs.

VI. CONCLUSIONS

Conclusions drawn from any study or effort are generally a combination of objective results and subjective inferences based in part on these results.

This SITE demonstration was conducted to determine the following:

- The effectiveness of the technology to solidify and stabilize waste materials found at the site.
- The ability of the solidified materials to maintain physical properties and structural stability over a five-year period.
- The change in volume and density of the solidified material after adding pozzolans, water, reagent, and other additives.
- Reliable capital and operating costs for use in the Superfund decision making process.

The results of this demonstration indicated that the process was effective in solidifying and stabilizing the waste streams on the site. The data indicate some noteworthy effects of using additives with high pH values, specifically, 1) testing procedures may need to be altered to accommodate pH range and 2) there appears to be an effect on phenols which are apparently selectively leached out of the matrix. Further study on these effects is currently being conducted.

The range of unconfined compressive strengths and low permeabilities verify the solidification objective. The objective of five years of testing hasn't been accomplished but one can infer that concrete is not likely to revert to basic constituents even though some cracking or spalling may likely happen.

The change in volume ranged from 0 to 60 percent but the median appears to be less than 30 percent. This is an important parameter when estimating disposal volume of treated waste and this level is probably an acceptable increase at this point in time.

Capital and operating costs of an intimate mixing operation or technique are also reasonable. Any treatment technology is going to add a significant cost to waste management over the no-treatment option. The objective is to optimize the treatment costs consistent with the risk the untreated waste may pose in the future. This should not be considered as an isolated parameter but rather by a systems approach to reducing environmental risks for the future.

This particular demonstration was successful in meeting the demonstration objectives. However, the SITE program itself has certain goals, four of which are listed below:

- To identify and remove impediments to the development and commercial use of alternate technologies.

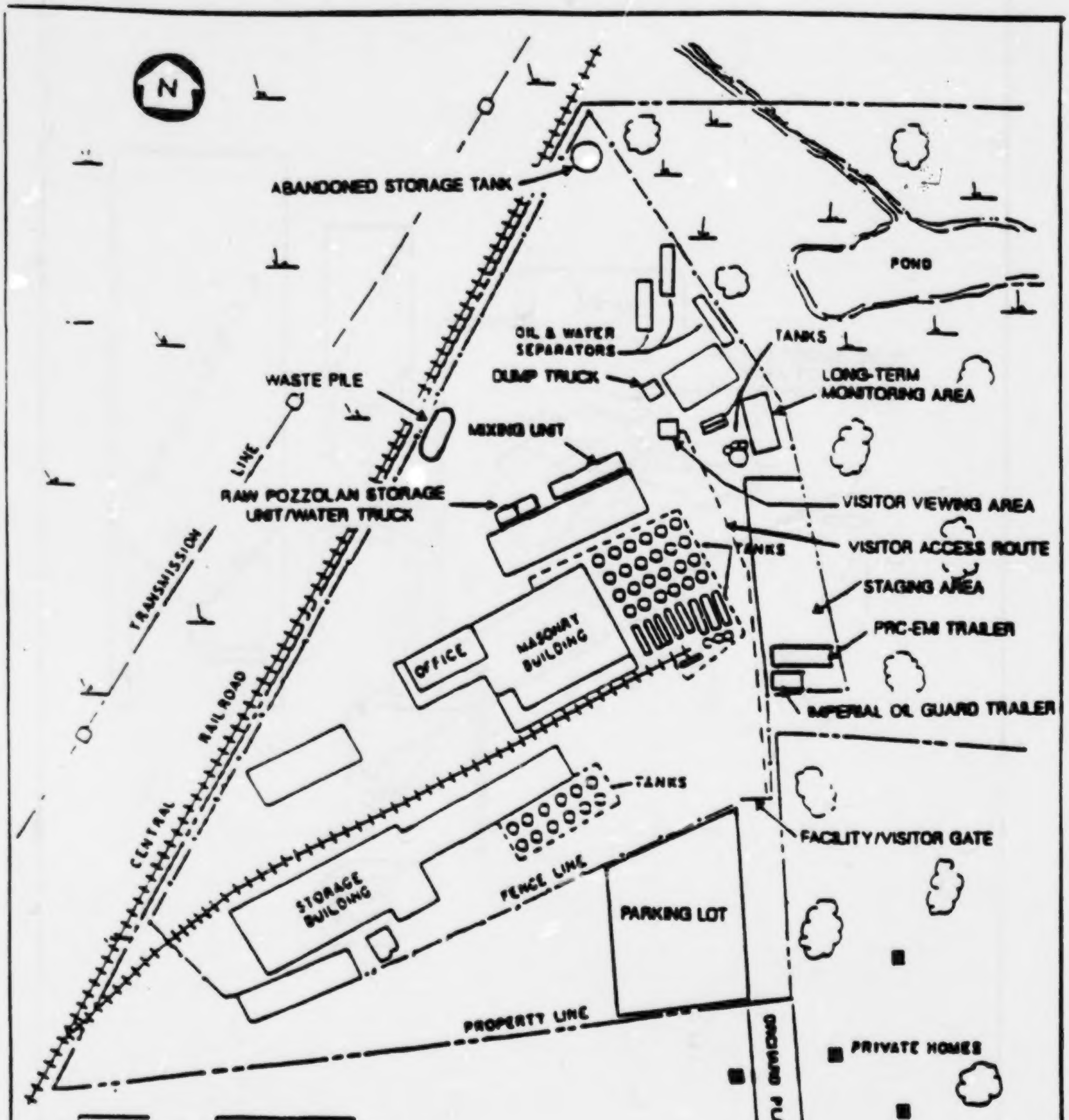
- To conduct a demonstration of the more promising innovative technologies to establish reliable performance and cost information for site characterization and cleanup decision-making.

- To develop procedures and policies that encourage the selection of available alternative treatment remedies at Superfund sites as well as other waste sites and commercial facilities.

- To structure a development program that nurtures emerging technologies.

For the most part, these goals, as they were applied to this project, we addressed successfully. Continued efforts must be made within the consultant industry and the "regulated" community to promote the use of these emerging technologies. Satisfactory approaches will not evolve if the program goals are not applied.

DEMONSTRATION LOGISTICAL AREAS AT THE IMPERIAL OIL FACILITY


N
ABANDONED STORAGE TANK
OIL & WATER SEPARATORS
TANKS
LONG-TERM MONITORING AREA
DUMP TRUCK
WASTE PILE
MIXING UNIT
POND
RAW POZZOLAN STORAGE UNIT/WATER TRUCK
VISITOR VIEWING AREA
TANKS
VISITOR ACCESS ROUTE
STAGING AREA
PRC-EMI TRAILER
OFFICE
MASONRY BUILDING
IMPERIAL OIL GUARD TRAILER
TRANSMISSION LINE
CENTRAL RAILROAD
TANKS
FACILITY/VISITOR GATE
STORAGE BUILDING
FENCE LINE
PARKING LOT
PROPERTY LINE
ORCHARD PLACE
PRIVATE HOMES
0
100
200 FEET

Staging area will contain clean equipment, supplies and toilet facilities.

FIGURE 1

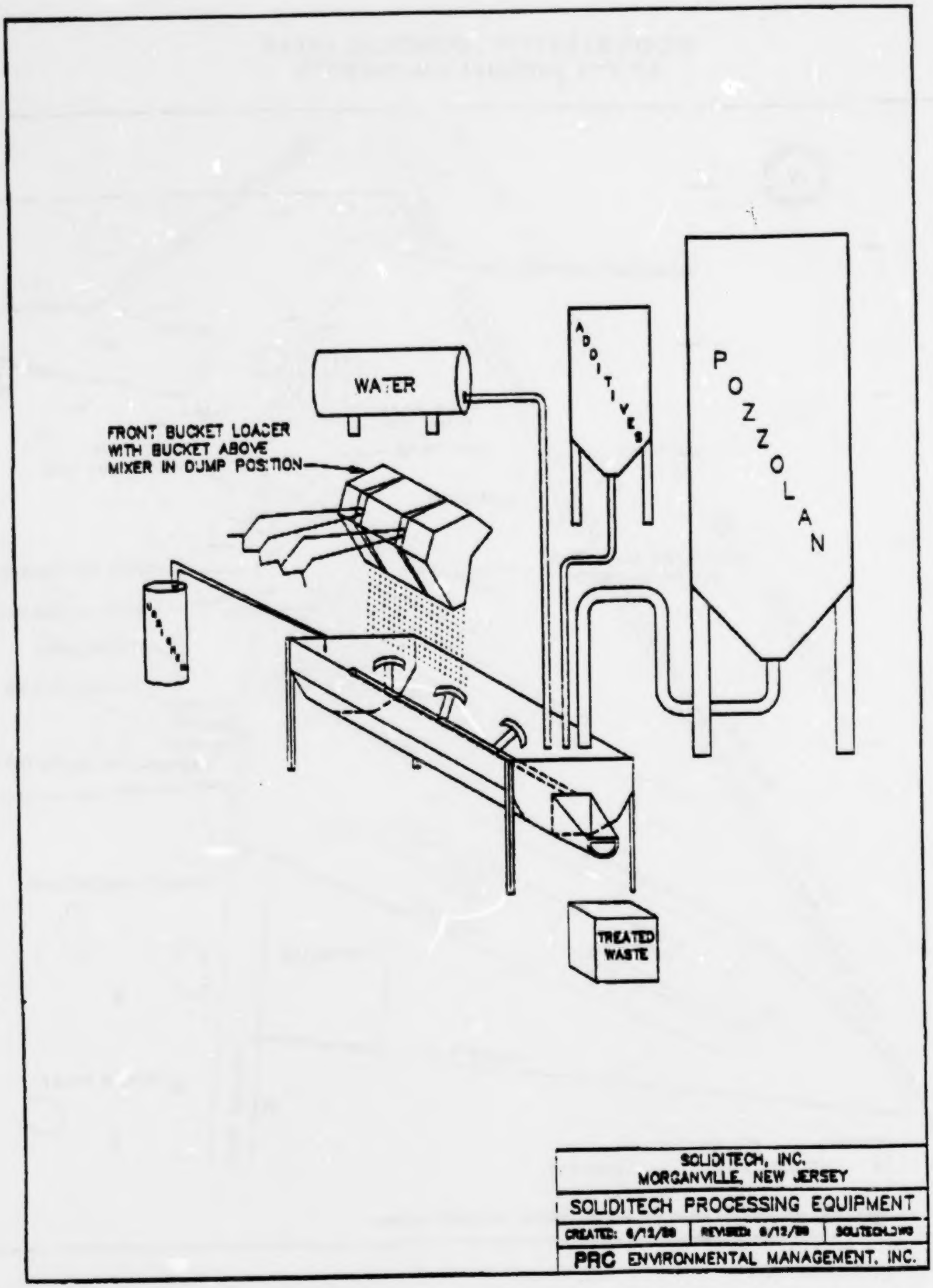

WATER
ADDITIVES
POZZOLAN
FRONT BUCKET LOADER WITH BUCKET ABOVE MIXER IN DUMP POSITION
TREATED WASTE
SOLIDITECH, INC.
MORGANVILLE, NEW JERSEY
SOLIDITECH PROCESSING EQUIPMENT
CREATED: 6/12/89
REVISED: 6/12/89
SOLITECH.DWG
PRC ENVIRONMENTAL MANAGEMENT, INC.

FIGURE 2

TABLE 1

PHYSICAL PROPERTIES

	Filter Cake		Filter Cake/Oily Sludge Mixture		Off-Site Area One	
	Untreated	Treated[a]	Untreated	Treated[a]	Untreated	Treated[a]
Bulk Density (g/cm^3)	1.1	1.4	1.2	1.7	1.3	1.6
Permeability (cm/sec)	NA[b]	4.5×10^{-7}	NA	8.9×10^{-9}	NA	3.4×10^{-8}
Unconfined Compressive Strength (psi)	NA	392	NA	856	NA	677
Loss of Ignition (%)	53.7	41.3	70.0	34.0	36.3	33.7
Water Content (%)	28.7	21.0	58.1	14.7	23.5	12.6

Notes:

[a] Treated waste sampled after a 28-day curing period.

[b] NA = Not analyzed.

TABLE 2

CHEMICAL PROPERTIES

	Filter Cake				Filter Cake/Oily Sludge Mixture				Off-Site Area One			
Chemical Analysis[a]	Untreated Waste	Treated Waste[b]	Leachate from Untreated Waste[c]	Leachate from Treated Waste[c]	Untreated Waste	Treated Waste[b]	Leachate from Untreated Waste[c]	Leachate from Treated Waste[c]	Untreated Waste	Treated Waste[b]	Leachate from Untreated Waste[c]	Leachate from Treated Waste[c]
pH	3.4	11.8	4.6	10.8	3.6	12.0	4.8	11.6	7.9	12.0	5.1	11.5
VOCs[d]	ND[e]	ND	0.27[f]	ND	50[f]	ND	1.3[f]	ND	10	ND	0.87[f]	ND
SVOCs[g]	ND	36[f]	ND	1.2	63[f]	17[f]	0.38	0.97[f]	79[f]	16[f]	0.12[f]	0.32[f]
PCBs[h]	28	16	ND	ND	43	15	ND	ND	43	40	ND	ND
Oil and Grease	170,000	77,000	1.4	4.4	130,000	60,000	1.6	2.4	28,000	46,000	1.9	12
Arsenic	26.4	28	0.005	ND	14	40	0.01	ND	94	92	0.20	0.02
Lead	2,200	680	4.3	0.002	2,500	850	5.4	0.01	650	480	0.50	0.01
Zinc	26	23	0.30	ND	150	54	1.3	ND	120	95	0.60	ND

Notes:

[a] Analyte concentration units for the untreated and treated waste are mg/Kg. Analyte concentration units for the leachate from untreated and treated waste are mg/L.

[b] Treated wastes were sampled after a 28-day curing period.

[c] Leachate values refer to results from TCLP test.

[d] VOCs = volatile organic compounds.

[e] ND = not detected.

[f] These values contain low levels of acetone, methylene chloride, various phthalates, or other analytes which are commonly attributed to sampling or analytical contamination.

[g] SVOCs = semivolatile organic compounds.

[h] PCBs = polychlorinated biphenyls.

ADVANCED CHEMICAL FIXATION of ORGANICS and INORGANICS/IN-SITU TREATMENT

By

JEFFREY P. NEWTON

INTERNATIONAL WASTE TECHNOLOGIES
WICHITA, KANSAS

INTERNATIONAL WASTE TECHNOLOGIES Inc.

Conceptual Basis of the Advanced Chemical Fixation (ACF) Technology

Waste treatment techniques that are composed of Portland cement, fly-ash, cement kiln dust, quick-lime, soil, clay, asphalt, sodium silicate, slag, gypsum, etc., in various combinations for solidification/stabilization (S/S) have been used for a number of years all over the world. Users and suppliers of these technologies have in some cases also used the term chemical fixation (CF) to define various compositions of these materials, possibly with the addition of trace compounds to accentuate their effectiveness with certain waste types. Whatever the terminology used, S/S or CF, particular compositions of these materials are the basis of the proprietary treatment products on the market. Certainly one of the major appeals of this class of treatment technology is the relative lower cost, if it is sufficiently effective for the waste types it is applied. S/S has been viewed by many in the environmental field as a physical or civil engineering process instead of a sophisticated chemical system. Tests for the effectiveness of treatment revolved around certain levels of physical changes in the "ante et post" treatment state."Successful" treatments of some metals, radioactive and non- radioactive, incertain concentrations in sludges, soils, and liquids as measured by particular light acid and water leach tests gave additional marketing credence to the notion that this was a viable and effective treatment for a wide range of waste types. Very little in-depth research of the chemistry and physics of S/S and CF as it applies to complex or mixed wastes was done because "it worked", as determined by certain static and dynamic, deionized water leach tests. Also the use of the CF term with various associated unsubstantiated or stretched logic claims as to a given product or compositions ability to treat a given waste effectively added another level of apparent creditability. In parallel to the use of S/S over the past few years there has been a somewhat erratic or wandering but yet evolving regulatory structure, influenced by an increasingly negative and dubious public opinion of the true effectiveness of S/S and CF and it's users. The environmentally active and concerned public elements, and to a increasing degree the regulatory authorities, saw no true distinction between S/S and CF except marketing hyperbola. In many groups, S/S and CF is viewed as "low tech, no-tech, or pseudo-tech" approaches to waste treatment. One important element needed to solve the effectiveness issue are the questions of what comprises a reasonable, realistic, or necessary test procedures of S/S and CF technologies and the "how clean is clean?" standards. The treatment evaluation methods and standards for S/S and CF are a point of contention among the users and marketers of S/S and CF, competing forms of treatment, the regulatory authorities, and the public.

In the midst of this complex scenario we have been doing research into the basic chemistry of chemical fixation of organics and inorganic toxic contaminated soils, sludges, and liquids for the past few years. We believe the necessary reality of S/S or more appropriately defined CF, involve exceedingly complex chemical mechanisms and phenomena. And this class of technology should be evaluated on such terms as to its true effectiveness. One of the major objectives of this article is to develop a definitional separation between the nature of S/S and CF using the HWT-20 Series (Patent Pending, IWT) compositions as the prototype of a new ACF class of treatment technology. In that regard we will review GC/MS readings of acid leach and solvent extraction tests of cases involving soils contaminated with PCBs and other high content mixtures of organics treated with the International Waste Technologies (IWT), HWT-20 Series Products. A recently discovered problem with high content organic wastes treated with a typical S/S mixture using a quick-lime, pozzolan base will be discussed. We have also used infrared adsorption (FTIR) and differential scanning calorimetry (DSC) to give insights into the chemical bonding mechanisms of this particular type of ACF technology with a range of organic compounds in a pure liquid or contaminated soil form. It would be wise at this point to give some background information relative to the chemical design and analytical thinking that went into the HWT-20 ACF prototype. As was implied earlier we believe that S/S and CF should be based on an accurate paradigm of the chemical process rather than a adsorption/dilution panacea judged effective by weak arguments of diffusion potential and end-state physical characteristics of questionable relevance and validity. Our position is that the extent and strength of the chemical bonding and alteration to innocuous forms within the treated matrix is a truer measure on the short and long term effectiveness of this category or form of treatment.

Chemistry Overview

This HWT ACF technology is based on three sets of interrelated functional chemical groups. There is a cement matrix chemistry, organophilic linking mechanisms, and a free radical and ion attack mode. The underlying concepts have been discussed in some intermediate level of detail by us in previous papers, so we will summarize this time.

Matrix Cement Chemistry: The objective of the cement chemistry is not primarily end-state physical properties but to facilitate the overall objective of bonding the toxic molecules and ions within a given contaminated material. In line with that point certain aspects of the cement hydration reaction (CHR) are altered and stretched out in time, the fibrils (sulpho-ferri-hydrates) that exist in the second stage of the CHR are modified to be more chemically reactive, and caused to be more dense. Certain admixtures are used to to cause a greater dispersion of the cement particles in impure environments which in turn will promote better development of the weak IPN (Interpenetrating Polymer Network) bonding function. This function is the slowest reaction of all three functional groups and its primary function is to be the silicate anchor matrix to which all other reaction products attach.

Free Radical and Ion Attack Chemistry This is a parallel chemistry that can be made up of a wide range of compounds that produce highly reactive ions and complexes in the HWT-20 slurry. This activity does not interfere with the functioning of the other major functional CF groups. This chemical function should attack various toxic organic and inorganic elements within the contaminated medium and reduce them to relatively inert forms or reaction products that can subsequently react with one of the other functional groups in the HWT-20 ACF material. A simple example of this capability is the use of transition metal complexes, but even these must be thought out carefully for one could cause certain counterproductive reactions. An example of this is shown in Figure 2, Coordination Complexes, and an explanation of the bonding is given in Figure 3.

Organophilic Linking Mechanisms These are intercalation compounds, such as modified smectite clays, that interact with the organics present, within certain ranges of predetermined selectivity, by a sorptive process in either of two general modes. The strong, short range bonding is based on a Bronsted and or Lewis acid or base reaction, see Figure 4 relative to such a reaction we have observed with triethanolamine. The weak, long range forces are basically hydrogen bonds, see Figure 1 induced dipole or Vanderwaals forces. There can be an initial reaction based on the weak force reaction and later a second strong or Lewis basereaction.

These modified smectite clays have both organic and inorganic properties due to the substitution in the normally inorganic clay structure of the Group IA and IIA metal ions that present with quarternary ammonium ions. This makes them ideal linking mechanisms between the toxic organics in the waste and the cement matrix. The introduction of the quarternary ammonium ions also opens the basal spaces in a pillaring effect to allow like polarity organics into the strong force reaction zone. Bonds can range from weak Vanderwaal forces to strong co-ordinate covalent bonds.

The important point is that this is primarily a problem in supramolecular chemistry and that multiple and secondary bonding and positioning of the appropriate molecular structures is the key issue. The individual FTIR shifts on functional groups seen are usually not considered large and in some cases are slight, but the number of bonds, the sum of the shifts, and the positioning of the bonds is a stronger effect in most cases one would see in a primary bond. An indication of the strength of this multiple and secondary bonding phenomena can be seen in "Percentage Increase in Energy" of the DSC analysis of a given waste. (Figure 4). We have also done DSC studies on the treatment of pure phenol, nitrobenzene, and trichloroethylene and achieved percentage energy increases of 220.7, 275.9, and 52.8 respectively. An significantadjunctcondition is that the behavior of a pure substance in a laboratory gives one an idea of what is possible but in a real, complex waste many other factors will interfere with the ACF material chemistry in achieving the maximum desired effect. There are some positive assisting factors but in most cases one must design ACF materials to overcome a variety of chemical hurdles before the fixation reaction can reach the desired level of efficiency. The use of advanced chemical techniques and analysis provide invaluable insights into the waste chemicalmechanisms.

Fourier Transform Infra Red (FTIR) FTIR studies are used to understand the extent of interaction between the toxic compounds and the HWT-20 ACF material. This analytic technique measures the changes in vibrational motion in specific bond relationships. It also helps to determine the functional elements present in a given molecule and involved in a bonding process.

DifferentialScanningCalorimetry(DSC) DSC measures the changes in temperature and energies associated with various significant chemical changes involved in bonding, such as the dH of melting, dH of evaporation, dH of decomposition, dH of phase transition, etc. This technique can indicate the strength of bonding.

OVERVIEW of IN-SITU APPLICATION

The application of the ACF technology can take place above ground level using a variety of mixing systems or in the ground, in-situ, as was done at the former General Electric transformer repair facility site in Miami, Florida. The use of high and or low pressure, rotary shaft injection with or without mechanical blade mixing has been done for more than ten to fifteen years in the construction industry for creating injection piles and sub-surface barriers. It was a natural extension of this construction method to be used in the treatment of contaminated soils and sediments, if one had a cement chemistry that would prevent both inorganics and organics from leaching at an unacceptable level. The low pressure, rotary shaft injection and blade mixing equipment offered by Geo-Con, Inc. was chosen because it would give an even, homogeneous blending of the HWT-20 ACF with the soil and subsurface porous limestone strata encountered at the site and create accurately placed, overlapping columns the entire length of the column. An additional purpose of the in-situ method other than the fact it treats the contaminated soil in-place is that GE was interested in using this technique of application in sites where there was volatile and semi-volatile organic contamination of the subsurface soils where it would not be desirable to expose these soils to the air by a removal technique.

At the SITE's Program Demonstration Geo-Con used a relatively small diameter drill, one yard, for two reasons. The drilling for most of the time was in rock and the objective was to prove the concept of in-situ treatment. The mixing drill process could be operated in sand/clay soils with a larger diameter drill (2 to 3 yards) and or multiple, parallel drills, up to four shafts quicker and more economically. In-situ treatment costs can be as low as $20 to 30/yard, excluding treatment chemicals, on a large project, up to $60 to 70/yard in difficult situations.

PCB LEACHING and EXTRACTION STUDIES

The HWT-20 CF Series was successfully used in the treatment of PCBs at the General Electric (GE) Miami Site under the U.S. Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) Program. This application was done in-situ using mixing drills down to 6.15 meters from Geo-Con, Pittsburgh. The first 1.2 m was sand, the second 2.5 m was a porous coral like limestone, and below that quartz sand, with fresh water at 1.2 m. The level of addition of the HWT-20 CF material was 15% by weight to soil. In other words for every metric ton of contaminated soil 150 kg of dry HWT-20 was added in a slurry form. The maximum concentration of PCB was 5700 ppm. The leaching procedure was the USEPA TCLP (Toxicity Characteristic Leaching Procedure), 18 hour dynamic acetic acid test, ANS 16.1, and the MCC-1 leach procedure. Essentially no PCBs came out in the EPA testing and only one sample was found to leach in GE's testing and that was 1.2 ppb on a two week old sample. GE did methylene chloride extractions of drill core samples as well and did not find in excess of 206 ppm PCBs in the treated samples using GC/ECD.

In some pre-project laboratory experiments carried out by Dr. R. Soundararajan gave some insights into what was occurring in the treated soil matrix. In a sample of similar type PCB contaminated soil, eight-hour methylene chloride extractions were performed on the untreated and crushed treated samples.

Analysis was done by GC/MS with the machine calibrated against all 221 position isomers of PCBs. In one sample of this experiment an admixture was included that produced a sulfurous acid that would totally disable the organophilic clay linking mechanisms between the PCBs and the slower developing silicate based anchoring matrix. In the second sample the admixture was removed so the primary linking mechanisms could function.

The results are as follows, untreated soil released 28,800 ppm PCBs in a methylene chloride extraction.

	Sample 1: Admixture	Sample 2: No Admixture
Treated Extraction	26,437 ppm	2,800 ppm
Treated TCLP	10,437 ppm	12.5 ppm

These tests were done only three days after treatment. A treatment dilution factor of 20% is included in above numbers. TCLP numbers did improve with the age of treated sample. This particular sample showed only a 5-6,000 ppm value using standard GC/ECD analysis mainly because the GC/MS could sort out all 221 PCB isomers. Also high values(40-50,000 ppm) of chlorinated benzenes were found, most likely the decomposition products of the PCBs, since no chlorinated benzenes were ever used at the site. They were reduced in a similar proportion to the reduction in PCBs of Sample 2 from untreated to treated extraction values. Almost all the existing PCB isomers after treatment were the low value chlorine forms.

The conclusions of the above experiment were supported further in another set of leach and extraction tests performed on a sample of a clay/sand soil contaminated with low levels of PCBs(290 ppm). The testing procedure was the same as above with the focus on which isomers were bonded or retained in the treatment matrix after a solvent extraction of crushed treated samples for eight hours. The TCLP leach tests of the treated material were all non-detectable. The sample cured for seven days. The treatment level of HWT-20 was 15% by weight to the weight of soil. In the untreated soil there was some chlorobenzenes and substituted phenols but none were found in the treated. Only the lighter PCB isomers (tri, tetra, and penta) were found in the treated. The hexa and heptachlorophenols were not found in the treated. The total PCB content extracted was 190 ppm or 65%.

Relative to PCBs the current HWT ACF treatment technology is able to alter or bond to a high degree the heavier chlorinated PCB molecules and a lessor degree the lighter chlorinated molecules. It is very effective in preventing the leaching of PCBs against the TCLP of all types. Also the HWT-20 ACF treatment sufficiently bonds and prevents the leaching of the PCB decomposition products, substituted benzene and phenols compounds. Newer formulations of a more advanced IWT ACF product show significantly greater rates of bonding or chemical alteration of organics including PCBs. An example of the treatment of a PCB containing waste with our newer "Polyfunctional Reactive Silicates" (PFRS) (TM) is shown in Figures 5 and 6. These ACF materials are based on new inorganic carceplex structures and heretofore non-existent organic trailers. As the results are shown it is are most effective PCB reaction to date and the research is continuing to be positive. The first of these new PFRS materials should be commercially available later this year.

Treatment by ACF of High Content Organic Waste

An organic content waste with a high percentage of heavy hydrocarbons with relative trace to small fractional loadings of volatile and semi-volatile toxic compounds is normally a difficult material for the usual S/S mixtures to effectively treat unless some integer multiple by weight of the S/S material is added to the weight of the waste and end-state physical properties are all that is being considered. The waste sample in this case was a soil with a heavy concentration of long chain hydrocarbons from a acid/clay process for recycling used oil. The major organic toxic components of this waste as determined by a solvent extraction and analyzed by a GC/MS were the following:

	Untreated Extraction	Treated Extraction	TCLP
Bis(1-chloro iso propyl) ether	8,528 ppm	ND	ND
Naphthalene	18,060 ppm	1445 ppm	ND
Phenanthrene	20,184 ppm	ND	ND
Benzo (A) anthracene	30,460 ppm	ND	ND

This contaminated sample was treated 50% by weight with a experimental and more advanced CF material and allowed to cure for only two days. This treatment level is too high for an actual project but what we were trying to achieve is an accelerated effect that would allow us to examine the bonding activity more quickly by the solvent extraction (GC/ MS), FTIR, and DSC analysis. A dilution factor of 50% was used in all quantitation. Standard methods of analysis and QA/QC were used.

With such a complex mixture to analyze by FTIR and DSC the approach has to be different then working with a pure known organic liquid. In using FTIR we focused on functional groups that we knew were there in relatively large concentrations and looked for shifts within those groups to indicate a level of bonding activity. In reviewing the data we have found that there were significant shifts in a number of FTIR frequency regions, hydrogen bonding was occurring between the aliphatic amines, hydroxy compounds, and the oxygens in A12O3 and SiO2 in the CF material. There was a amine salt formation as the result of a Lewis base reaction at 1580 cm-1. The most significant shift occurred at 1005 cm-1 where a hydrogen bond was formed with an SiO2. This is explained by the fact that the oxygens of the silica strongly interact with the hydrogens of alkyl, hydroxyl, and amino groups which results in a reduction of the O-Si-O bond order. (Table 1, Infrared Data)

The DSC data (Table 2, DSC Data) also confirms that relatively significant bonding activity is occurring. The dH of vaporization has increased by 54.9% from untreated to treated. The DSC analysis is a energy summation function rather than a focus on a specific reaction.

Recent experimental work done by Dr. R. Soundararajan has indicated that lime, lime/fly-ash, or pozzolan based S/S of organic content waste of a sufficient level, what this threshold is is not known yet, but certainly the oil recycling waste in this case applies, will generate significant carbon monoxide and or acetylene gas when exposed to water of even mild acidity. Also during the process of S/S or CF treatment it is desirable to keep the heat generation by the reaction with water as low as possible since the more heat generated the more the volatilization of the organics. The IWT ACF technology does not contain but trace amounts of lime in the cement used in a fraction of it's composition and no pozzolans are used. The rate of addition of the IWT ACF materials used to weight of waste is relatively low, 12 to 20%, and has a lower heat of hydration than straight cement.

Summation

Chemical fixation technology is far more advanced and cost/effective than most people realize, especially from those companies or groups that have done in-depth chemical research of the basic fixation reaction mechanisms. International Waste Technologies has and is doing this basic research and believes that the HWT ACF Product Series and the new, more advanced products, PFRS, that will come out in the near future will compete favorably with thermal and biological methods in the destruction, alteration, and or bonding of organics and the immobilization of inorganics. The effectiveness of ACF technology can be verified analytically with relative quickness and function in a wide range of contamination environments at relatively acceptable costs and ease of use factors. An important key to the success of this category of toxic waste treatment is for the regulators and users of this type of technology insist on high standards of relevant chemical testing and verification in the pre-project treatability analysis and careful QA/QC during project application.

In-situ applications that are effective in terms of their homogeneity of mixing of the ACF material with the contaminated soil to the required level and do not leave any voids can be an effective, economical, and necessary part of the waste treatment picture. The Geo-Con system successfully demonstrated that objective.

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J. P. Newton - June 7, 1989
International Waste Technologies, Inc.
150 North Main-Suite 910
Wichita, Kansas 67202
316-269-2660, Fax-316-269-3865

TABLE 1

INFRARED DATA

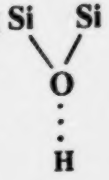
Waste Extract cm -1	Waste Extract + Binder cm -1	Infrared Frequency Shift cm -1	Infrared Functional Group Assignments
3394	3385	-9	OH Stretch O- - -H....O
3382	3372	-10	NH Stretch N- - -H....O
3373	3355	-18	
1597	1580	-17	Keto group C::::O....H
1035	1005	-30	Hydrogen Bonding 

TABLE 2

DSC DATA

DSC Endothermic Peak Values

	Temperature (Degrees C)	H (Vaporization) Cal. per gram
Waste Extract	138.90	18.63
Waste Extract + Binder	121.2	6.15
	414.4	2.32
	414.5	2.06
		10.53 Total

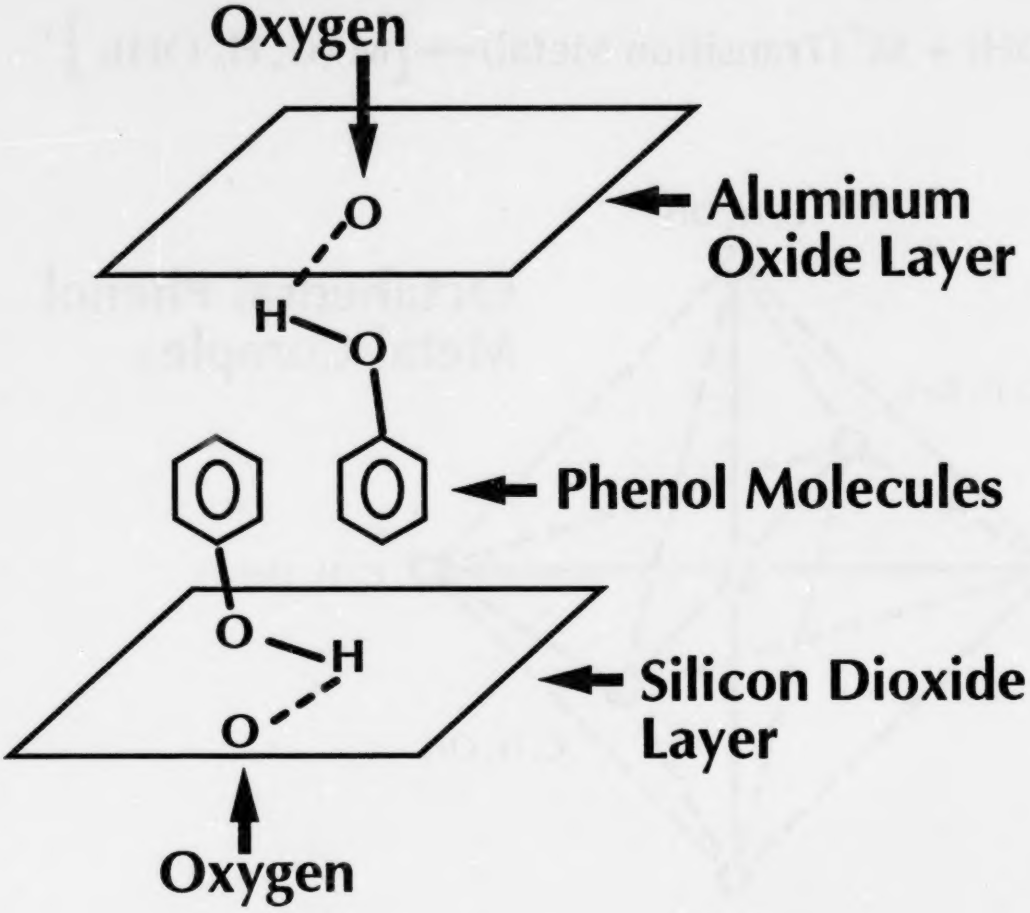
	Waste Extract Cal/gram	Waste Extract + Binder Cal/gram
Total H (Vaporization)	18.63	10.53
Total H (Vaporization) corrected to 100%	---	28.65

	Waste Extract + Binder
TGA - Percent wt. loss at given temperature range	36.48
PERCENT INCRESE in H (Vaporization) for Waste Extract + Binder	54.9

FIGURE 1

Observed Bonding Phenomenon in the HWT-23 Treatment Matrix

Hydrogen Bonding of Phenol Molecules



Oxygen

Aluminum Oxide Layer

Phenol Molecules

Silicon Dioxide Layer

Oxygen

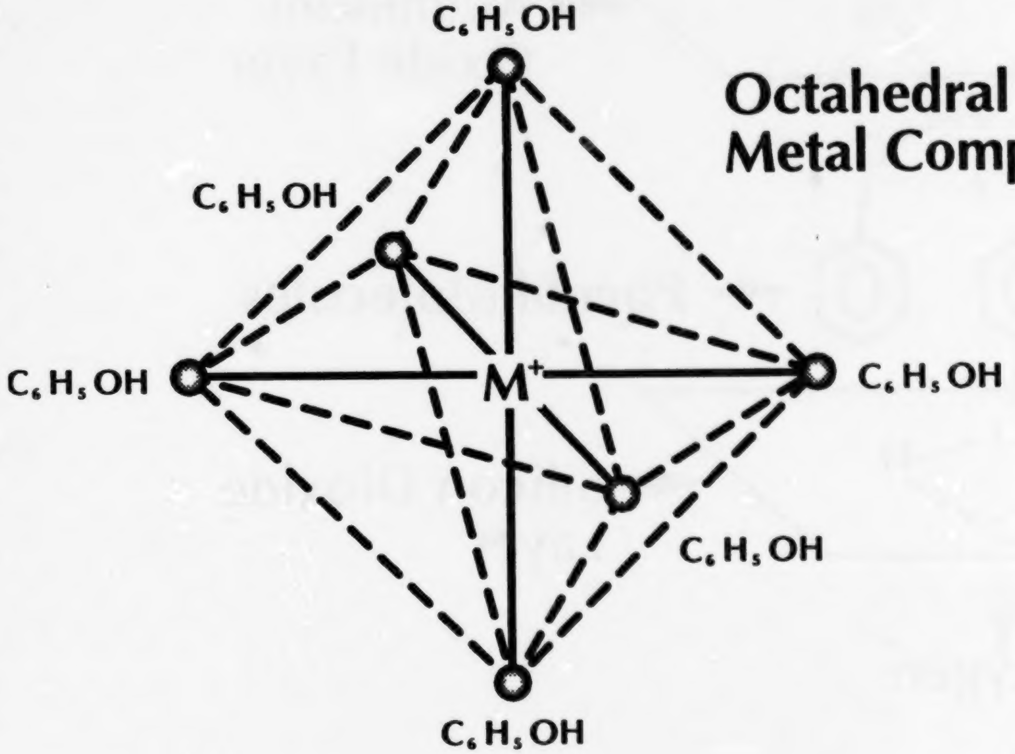
Evidence:
Lowering of FTIR Stretching Frequency

Phenol	Treated Phenol	Shift	Peak Assignment
962 cm^{-1}	934 cm^{-1}	-28 cm^{-1}	C - O
3640 cm^{-1}	3632 cm^{-1}	-8 cm^{-1}	H - bonded OH

FIGURE 2

Coordination Complexes

$$6\,(C_6H_5OH) + M^{3+}\text{(Transition Metal)} \rightarrow \left[M\,(C_6H_5OH)_6\right]^{3+}$$

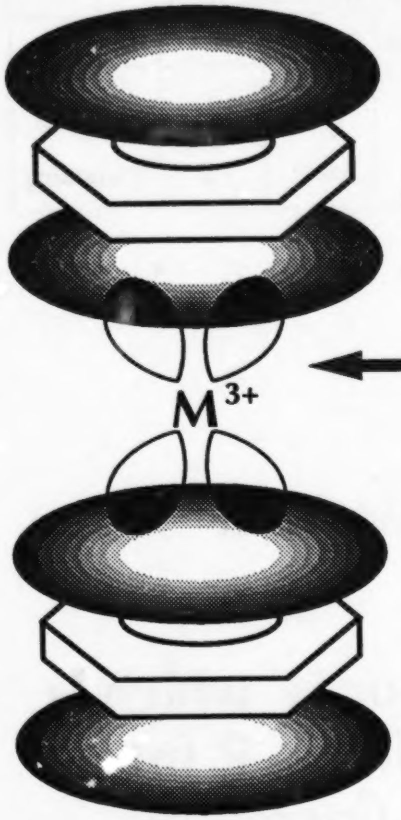

C_6H_5OH
C_6H_5OH
C_6H_5OH
M^+
C_6H_5OH
C_6H_5OH
C_6H_5OH

Octahedral Phenol Metal Complex

Evidence:
UV - Visible Spectra - Drastic Color Change

FIGURE 3

Pπ to dπ Bonding



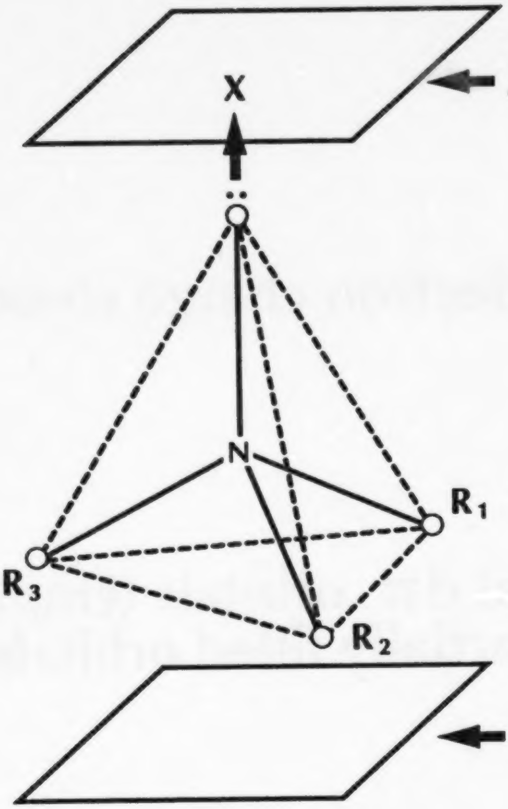
← π Electron charge clouds

← Metal dπ orbitals (empty or partially filled orbitals)

Evidence:
Shift in FTIR Frequency for Ring Breathing

FIGURE 4

Lewis Acid Base Reactions: Formation of Sigma Bonds (σ)



FTIR ANALYSIS			
Triethanolamine	Treated	Shift	Peak Assignment
2104	2297	193	Amine Salt Formation
1075	1070	- 5	H bonding

X ≡ Electron deficient species or H^+ which is a Lewis Acid. Evidence: Shift in N - R (n) frequency in positive direction (increase)

DSC ANALYSIS - TRIETHANOLAMINE

Edotherms (°C)	H of vaporization (literature) Kcal/mol	Observed H of vaporization Kcal/mol	Percentage Increase in energy	Boiling point (°C)	Highest endothermic temperature (°C)
150.97 337.30	12.78	24.16	89.0	335.4	337.30

FIGURE 5

Formation of Permanent $\sigma+\pi$ Bonding (Covalent Bonding)

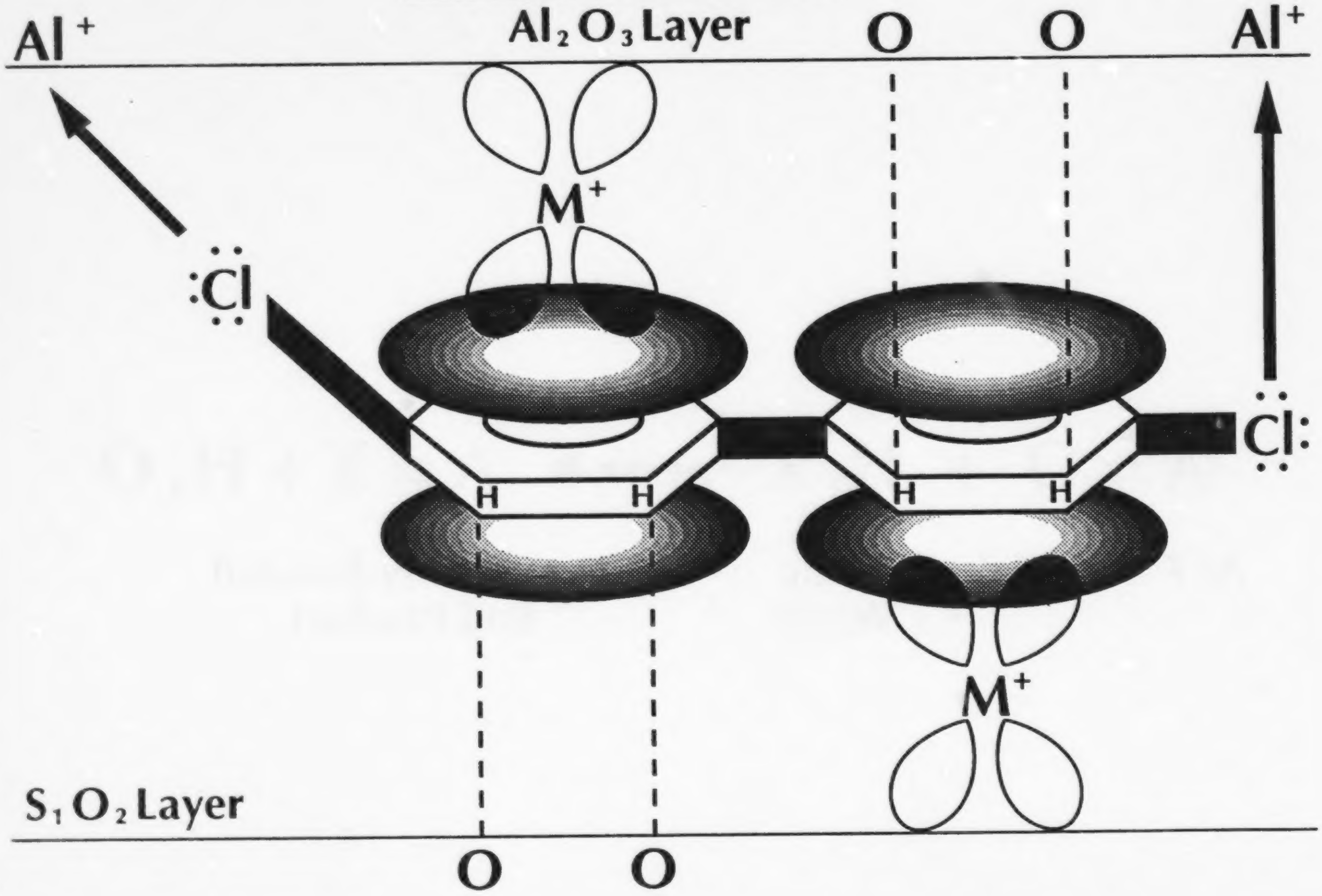
$$A = O + H_2X \longrightarrow A = X + H_2O$$

ACF Material	Toxic Waste	Irreversibly Bonded End Product

FIGURE 6

Supramolecular Chemistry/ Multiple and Secondary Bonding

Dichlorobiphenyl


Al+
Al2O3 Layer
O
O
Al+
M+
:Cl
Cl:
H
H
H
H
M+
S1O2 Layer
O
O

Solvent Extraction and Leach Results:

	Untreated (ppm)	Solvent Extraction of Treated (ppm)	TCLP
PCB	17,580	N.D.	N.D.

FTIR Study of PCB

Dichlorbiphenyl	Treated PCB	Shift	Peak Assignment
1150 cm^{-1}	1118 cm^{-1}	-32	Cl to Al Coordinate Bond

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